ANNUAL REPORT

OF THE

PROGRESS OF CHEMISTRY,

And the Allied Sciences,

PHYSICS, MINERALOGY, AND GEOLOGY,

Including the applications of Chemistry to Pharmacy, Medicine, Agriculture, the Arts and Manufactures.

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ADVERTISEMENT.

The great and daily increasing number of researches appearing every year in the different departments of Chemistry and the Allied Sciences, renders it difficult for individuals to obtain, by actual inspection of the original sources, a complete survey of their progress.

The study of *one*, or even of several journals, does not suffice for this purpose, the communications of various investigators being distributed over a large number of periodicals, and many papers, especially interesting to the Chemist, being actually buried in publications chiefly devoted to other subjects.

It is evident that a rapid acquirement of an accurate knowledge of the progress made by so extensive a Science as Chemistry, and a clear perception of the connexion of the individual researches as to their confirmation, correction, or refutation of each other, would be most materially facilitated by an Annual Report, founded on the broadest possible scientific basis, and carried out by men equal to the task.

Professor Liebig, in conjunction with several distinguished scientific men, has undertaken the regular publication of such an account. By the united activity of a number of persons working on a well-connected plan, it will be possible to obtain a detailed account of the researches published during each succeeding year, soon after its expiration. The Report of the Progress of Chemistry and the Allied Sciences will always be in the hands of the scientific public before the middle of the following year.

The labours in the field of Chemistry, including its application to Pharmacy, Medicine, Agriculture, the Arts and Manufactures, will be reported with minute accuracy, it being intended to insert a faithful, and, whenever necessary, a complete digest of each investigation.

The part of the work devoted to Physics and Mineralogy will form a complete synopsis of the literature; while a detailed account will be given of such subjects as are of particular importance to the Chemist.

In Geology, which has of late derived so many advantages from the progress of Chemistry, the discussion will be extended to all inquiries instituted on the boundary line of the two Sciences.

The Annual Report aims at completeness, principally in the communication of *results;* descriptions, however, of *methods*, by means of which these results may have been obtained, will be by no means omitted, whenever it may appear conducive to the comprehension of the subject, or whenever the methods themselves are new.

One of the principal objects will be to treat synoptically of the different researches published on the same subjects, and to expose in a lucid manner the relation existing between recent inquiries, and our actual store of knowledge; it is not intended to give merely isolated and unconnected abstracts of the several individual investigations.

By experience and researches of their own, the Authors of the Annual Report will be frequently enabled to point out such questions as require confirmation or correction, or to which, up to the present moment, due attention has not been accorded: criticism likewise cannot altogether be excluded.

This Series of Reports commences with Two Volumes, extending over the years 1847 and 1848; each future Report will be limited to one year.

CONTENTS

OF THE

FIRST VOLUME.

PHYSICS AND PHYSICAL CHEMISTRY.

MOLECULAR ACTIONS.

ATOMOLOGY.

THERMOLOGY.

KINETICS.

(SCIENCE OF MOTION).

ACOUSTICS.

OPTICS.

MAGNETISM.

ELECTRICITY.

INORGANIC CHEMISTRY.

CONTENTS.

ORGANIC CHEMISTRY.



PHYSICS

AND

PHYSICAL CHEMISTRY.

MOLECULAR ACTIONS.

It is well known that the state of all bodies is dependent upon the mutual action of two forces, the one, *molecular attraction,* which appears to be essentially a property of ponderable matter; the other, *molecular repulsion,* which may be considered as a manifestation of the caloric enveloping the smallest particles of bodies. The resultant, in every case, of these two forces, is what in fluids and solids is called the force of cohesion.

Cohesion of liquids, and capillary elevation dependent on the temperature.

Cohesion of Liquids, and capillary Elevation dependent on the Temperature.—It has long been known, that the cohesion of fluids is diminished by an increase of temperature. With the part, however, which the caloric plays in this change we have been till recently almost unacquainted. This change could be attributed to an increased thermal tension, just as well as to a diminished density, for the molecular attraction as a property of mass must vary with the square of the density. In their theoretical investigations on capillary phenomena, and on the cohesion of liquids closely connected therewith, La Place and Poisson, neglecting as insignificant the increase of repulsion, have, in fact, exclusively considered the diminution of the density.

The latest experimental researches have concordantly proved, that cohesion, at least within the limits of our present observations, is not perceptibly influenced by an increase of the distance between the ultimate particles, whilst its diminution sensibly keeps pace with the increase of temperature.

Direct measurements of the changes effected by heat in the cohesion of some liquids, have been communicated by Buys-

Cohesion of liquids, and capillary elevation dependent on the temperature.

Ballot(1). He employed, in his experiments, adhesion-plates of glass and metal.

A level plate, suspended from the one arm of a delicate balance and horizontally adjusted, was brought into contact with the surface of the liquid. The weight requisite to be attached to the other arm, in order to remove the plate from the liquid, afforded a measure of the cohesion of a section corresponding to its surface. Impurities, as likewise air bubbles, that might have got between the two surfaces, were most carefully removed, and altogether, it appears that every precaution necessary in such delicate experiments was attended to. The horizontal adjustment of the square plates succeeded best by means of three fine screws, admitting of lengthening and shortening the three cords of suspension.

The liquid to be examined was first warmed, and then, whilst slowly cooling, a number of experiments were performed in rapid succession between slightly varying temperatures.

With the rise of temperature up to 90° C., above which the observations were no longer accurate, a very regular diminution of cohesion was exhibited, capable of being expressed by an equation $p = \alpha - \beta t$, applicable to all the liquids investigated, p representing the weight necessary to separate the plate from the liquid, t the temperature, α and β being constants specially to be determined for every liquid.

The following table gives a synopsis of the principal results; in the column p we find, expressed in grammes, the weight requisite to separate a plate of 1 Sq.C. (centimetre) surface, representing the cohesion of a Sq. C. section of the liquid. By dividing p by the weight of 1 CC. (cubic centimetre) of the liquid, and multiplying by 10, we obtain, expressed in millimetres, the height to which the fluid in contact with the disc can be elevated above the level of that in the trough before the plate separates. This table, likewise, exhibits a result which is certainly remarkable, namely, that the cohesion of water is not only diminished by heat, but also by the introduction of soluble substances:

	Density at 0°.	$p = \alpha - \beta t$.
Water 10°—40° C.	1·000	0·5568—0·00108t
,, 17°—94° C.	1·000	0·5607—0·00110t
Solution of Glauber's salt	1·065	0·5100—0·00136t
,, ,,	1·160	0·5051—0·00073t
Solution of sulphate of copper, pure	1·212	0·5460—0·00080t
,, ,, ,, acid	1·125	0·5095—0·00085t

The numbers given by Buys-Ballot for water, and especially

(1) Pogg. Ann. LXXI, 177, abstract from "Dissertatio inauguralis de Synaphia et Prosaphia;" Trajecti ad Rhenum, 1844; a correction of his calculation by R. Merian in Pogg. Ann. LXXIII, 485, also in Arch. Ph. Nat. V. 355.

those for lower temperatures, tally tolerably well with the indications of other physicists obtained by very different methods, well enough, indeed, to dispel the objections raised by Donny(1). Nevertheless, the values in the foregoing table can only be regarded as approximative, as Buys-Ballot himself acknowledges; the method with adhesion-plates admitting scarcely of a very high degree of accuracy even in the hands of the most skilful experimenter; others have, therefore, preferred deducing the cohesion of fluids from their elevation in capillary tubes, a method to which, as is well known, the way was paved by La Place, who first succeeded in reducing the capillary phenomena to the force with which solid surfaces adhere to liquids.

Cohesion of liquids, and capillary elevation dependent on the temperature.

Within the last few years voluminous memoirs have been published by C. Brunner(2), and by Frankenheim(3), on the deportment of fluid bodies in capillary tubes. Those of the latter refer to experiments made previously, in conjunction partly with Sondhaus(4) and partly with Hildebrand.

Frankenheim introduced the liquids to be examined into syphon-shaped tubes, one limb being of a capillary, or at least of an exceedingly small bore, whilst the radius of the other varied from 3—7 millimetres. These tubes were immersed in a transparent bath capable of being heated, in order to produce the requisite variations of temperature.

Brunner has essentially followed the method of Gay-Lussac, which is described in Biot's 'Traité de Physique 1, 441.' He endeavoured to produce the required changes in temperature, by placing the glass cylinder, filled about one fourth with the liquid, in a tin vessel, having double sides, but through which a narrow groove, four lines in width, was cut, so as to allow of observations being made. This metallic vessel, which could be heated by a spirit lamp, was filled with oil. Both physicists observed the variations in height by means of a vertical rule fixed at a distance of some feet from the apparatus, with an appropriate telescope attached to it, capable of remaining parallel with its original position, while moving either up or down.

It is evident that the former method is more likely to secure the production of a fixed temperature, and an equal distribution of the

(1) Pogg. Ann. LXVII, 564.

(2) Pogg. Ann. LXX, 481; Arch. Ph. Nat. IV, 121. Ann. Ch. Pharm. LIV, 140 (in abstract).

(3) Pogg. Ann. LVII, 178; Arch. Ph. Nat. VII, 122 (in abstract); Ann. Ch. Pharm. LXIV, 143.

(4) J. Pr. Chem. XXIII, 401.

Cohesion of liquids, and capillary elevation dependent on the temperature.

heat, throughout the liquid to be tested, than Brunner's plan; the latter has the advantage of admitting of much more accurate measurement, an advantage the more apparent, if we consider that Frankenheim, unable to neglect the capillary influence altogether, even in the wide limb of his tubes, was nevertheless without the means of accurately correcting it.

Both physicists, however, find that the capillary elevation decreases with the temperature, and is capable of being represented by a very simple formula of interpolation, as a function of the temperature.

These formulæ, together with the limits of temperature, within which they are strictly correct, are arranged in the following table, which gives the height of the capillary column for a cylindrical tube of 1 millimetre radius, and for a temperature of 0°. In these determinations, the weight of the meniscus is introduced into the calculation, by assuming it to be equal to that of a liquid cylinder of ⅓ of the height of the radius. We have accordingly:

$$H = r\left(h + \frac{r}{3}\right)$$

H representing the height of the capillary column in a tube of 1 millimetre radius, and measured from the surface of the liquid to the lowest point of the meniscus(1).

	Sp. gr. at 0°.	Frankenheim H^{mm}.	Brunner. H^{mm}.
Water	1·0000	15·336—0·02875t or 15·336 —0·02751t—0·000014t² between 2°·5 and 93°·4 C.	15·332—0·0286t between 0° and 82° C.
Ether	0·7370	5·400—0·0254t between—6° and 35°.	5·351 — 0·0280t between 0° and 35°.
Olive oil	0·9150	. . . . . .	7·461—0·0105t between 15° and 150°.
Turpentine	0·8902	6·760—0·0167t between 17° and 137°.	
Oil of lemons	0·8380	7·23—0·0174t betw. 17° and 125°.	
Petroleum	0·8467	6·896—0·0151t between 17° and 128°.	
Alcohol	0·8208	6·05—0·0116t—0·000051t² between 0° and 75°.	
Spirits of wine	0·9274	6·41—0·0120t between—2° and 70°.	
Bisulphide of carbon	1·2900	5·10—0·0101t between—5° and 36°.	
Acetic acid	1·0522	8·51—0·0097t between 13° and 100°.	
Solution of chloride of zinc	1·3638	10·06—0·0220t between 40° and 85°.	
Sulphuric acid	1·8400	8·40—0·0153t—0·000094t² between 12° and 90°.	

(1) Biot, Traité de Physique, I, 449.

Frankenheim and Brunner have, as is seen, obtained almost the same values for water and for ether. For the former, Gay-Lussac had found $H = 15^{mm} \cdot 135$ at $8^0 \cdot 5$ C. Frankenheim's formula gives, at the same temperature, $15^{mm} \cdot 101$, that of Brunner $15^{mm} \cdot 089$. Cohesion of liquids, and capillary elevation dependent on the temperature.

The specific gravities annexed in the table show how little may be inferred from the density of a liquid, as to the cohesion existing amongst its particles. Generally it is true, that with the diminution in density of a liquid, there is also a diminution in the capillary elevation, but in a very different ratio; compare, for example, the average-diminution in the density of water and oil of turpentine, as represented by the formulæ:

$$1 \cdot 000\,(1 - 0 \cdot 00418t) \text{ and } 0 \cdot 8092\,(1 - 000886t)$$

with the corresponding variations of the capillary elevations of the same liquids, as expressed by the formulæ:

$$15{,}336\,(1 - 0 \cdot 001875t) \text{ and } 6 \cdot 76\,(1 - 0 \cdot 002466t)$$

In the same manner it has been found with other liquids, that the capillary elevation diminishes much more rapidly with an increase of temperature than would correspond to the diminution of the density.

The most conclusive proof, however, that the variations in density stand in no direct relation to the capillary elevation, is afforded by water at a low temperature. For whilst it exhibits a maximum density at 4^0, Sondhaus, and likewise Brunner, have found that an almost regularly progressing depression of the capillary column takes place with an increase of temperature even from 0^0 upwards.

Frankenheim, availing himself of Poisson's formula:

$$p = \pi\, r^2 \mu \sqrt{2\, a^2} - \frac{\pi\, r\, \mu\, a^2}{3}$$

expressing the relation of the capillary elevation to the cohesion of the liquid, has calculated the thickness and the weight of the liquid layer suspended between the adhesion-plates and the surface of the liquid at the moment of separation. He has, however, neglected in this calculation the second term $\frac{\pi r \mu a^2}{3}$; this is not admissible. The numbers which he has found cannot, therefore, have claims to absolute correctness, nor are they comparable with each other.

In the above formula $a^2 = \frac{H}{100,}$ *i. e.* equal in millimetres to the elevation of the liquid in a cylindrical tube of 1^{mm} radius, divided by

Cohesion of liquids, and capillary elevation dependent on the temperature.

100; μ represents the weight of 1 cubic centimetre of the liquid in question, πr^2 the superficial contents, in square centimetres, of the adhesion-plates, p the weight (in grammes) necessary to effect separation.

If we now calculate p for different temperatures, substituting always the corresponding values for μ and a^2, and availing ourselves of Brunner's formula for water, we shall arrive at a numerical series generally expressed by the equation

$$p = 0{\cdot}4632 - 0{\cdot}000358t - 0{\cdot}000002t^2$$

in which p represents the cohesion of water for a section of 1 square centimetre. Thus we find p to be 0·4632 grammes at the temperature of freezing water, and 0·4086 grammes at 100°.

According to Frankenheim's method of calculation, it will be for the same temperatures, 0·5544 and 0·4784.

It is well known that water, under sufficient pressure, can retain the liquid state, *i. e.* cohesion amongst its particles, at temperatures far above 100°. If we are justified in assuming that the formula just propounded will hold good also, at least approximately, for such higher temperatures, we shall be enabled to trace the cohesion diminishing with the rise of temperature to a point, where it will be balanced by a caloric repulsion of an equal intensity; we find that this must take place at 400°, *i. e.* water heated up to this temperature should, by the slightest increase of tension, by the introduction, for instance, of a single bubble of air, be suddenly, and throughout its entire mass, converted into steam. Moreover, as water, in order to be converted into steam, requires 610 heat-units, starting from 0°, it may be inferred that a very rapid increase of its specific heat will take place at temperatures above 100°.

Donny(1) has shown, by a series of well devised experiments, that water possesses a tendency to evaporate only when exposed to a vacuum, or a space filled with gas, and that the process of ebullition is induced by the air alone, which is present in the water. He succeeded in heating water, previously freed from air with great care, to 135° without inducing ebullition.—His experiments certainly prove, in a most convincing manner, that a space filled with gas or a small bubble of air, is absolutely necessary for the evolution of steam in the body of the water, and that accordingly, the process of ebullition in its principle, coincides with that of evaporation; in the further conclusion,

(1) Ann. Ch. Phys. [3] XVI, S. 167; Pogg. Ann. LXVII, 562.

Cohesion of liquids, and capillary elevation dependent on the temperature.

however, namely, that the cohesion of water was equivalent to the pressure of several atmospheres, he is certainly in error. In fact, no very great excess of cohesion is required to suspend in the body of the water the tendency to evaporate, which is nothing more than a preponderance of the repulsive power; for this purpose, the very slightest preponderance of cohesion is sufficient. It is true, Donny also supports his view on the well known fact, that fluids suspended in barometer-tubes sometimes do not descend in them, even when the open end is under the exhausting power of the air pump. It appears, however, that Donny, in explaining these phenomena, has not sufficiently considered the influence of the sides of the tube. The experiment would not have succeeded in wider tubes.

Holtzmann(1) has endeavoured to determine the cohesion of water, at different temperatures, by comparing the mechanical effect of the steam generated both with that deduced from the number of heat-units consumed, and with the mechanical effect of the unit of heat as ascertained by other considerations. The difference found was attributed to the heat required to overcome cohesion. In this manner, he arrived at the formula 607 — 1·1394t, which expresses, in units of heat, the cohesion of the weight-unit of water at different temperatures.

By dividing this expression by 607, and multiplying it by 15,332, we obtain 15·332—0·02878t being almost exactly the same value which Brunner had found for the elevation of water in a capillary tube of 1^{mm} radius. Holtzmann regards this coincidence as firmly supporting the correctness of his theoretical views. He has, however, in calculating the formula, assumed the specific heat of water to be constant, which, for the higher temperatures, is certainly not admissible. Again, he has taken the vapour-heat of water as equal to 640, which is probably too high. As the coefficient of the expansion of steam, he uses the number $\frac{1}{236}$; but Regnault has since proved by experiment, that even at a maximum density, it cannot differ much from that of air = $\frac{1}{273}$. The coincidence of the formula with that of Brunner is hence found to be accidental. And this cannot be well otherwise, since Brunner's formula, although well adapted to deduce the cohesion of the water, is nevertheless not a directly comparable expression of the cohesion.

A. Moritz(2), of Dorpat, in determining the resistance of water

(1) Ueber die Wärme und Elasticität der Gase und Dämpfe, Mannheim, 1845, abstracted in Pogg. Ann. LXXI, 463; Arch. Ph. Nat. V. 357; Ann. Chem. Pharm. LXIV, 147.
(2) Pogg. Ann. LXX, 74; Arch. Ph. Nat. IV, 391.

Cohesion of liquids, and capillary elevation dependent on the temperature.

at different temperatures, availed himself of a method described by Coulomb, which consists in observing the diminution of the rotary oscillations of a metallic disc suspended horizontally in the liquid, by means of a fine wire, and rotating round its centre under the influence of torsion. He found that, with the maximum density of water, the resistance was likewise at its maximum, but that it gradually diminishes with the rise of temperature, and in a much more rapid ratio than the density of water. His experiments are represented within the very narrow limits of from 2·5° to 23° R. by the formula:

$$c = 0{\cdot}2513 - 0{\cdot}01118t + 0{\cdot}0001387t^2 - 0{\cdot}000003258t^3.$$

This resistance evidently depends on the cohesion, without however being proportional, as Moritz appeared to believe. It rather corresponds to the resistance offered to fluids in their passage through tubes, which, as is well known, is not caused simply by cohesion, but essentially by the unequal intensity of this force, when exerted in different directions, *i. e.* by the degree of fluidity. This perhaps explains the striking discrepancies of these results, and those already detailed.

Change in Form of the Surface of a Liquid by another one.—Wilson(1) has observed that chloroform, when placed in a clean glass vessel, exhibits a concave surface, which becomes convex on the addition of either pure or of slightly acidified water, and level when a solution of an alkali is poured upon it. Drops of chloroform, on a level surface under water, are instantly compressed and flattened on addition of an alkali, and instantly reassume their original form when the alkali is saturated with an acid. Chloroform sinks very slowly in pure or acidulated water, but with great rapidity in an alkaline solution, Dutch liquid, bisulphide of carbon; the volatile oils heavier than water, behave similarly to chloroform, the latter however exhibits these phenomena most strikingly. Swan(2) has endeavoured to follow up this subject theoretically; we perceive from his research, that he found the surface of chloroform, when under alkaline water, to be level, excepting at the sides of the glass vessel where it was convex; olive oil and sperm oil, when floating on pure water or on water slightly acidified with hydrochloric acid, exhibit a convex undersurface, which is levelled on addition of an alkali; the same takes place with oil of lavender on the addition of alcohol. The convex surface of oil of cassia, under water, becomes level on the addition of either an alkali or of alcohol, that of oil of cloves by alcohol.

(1) Chem. Soc. Qu. J. I, 174. (2) Phil. Mag. [3] XXXIII, 36.

Swan gives the following determinations of capillary elevations—A representing the specific gravity, B the diameter of the glass tube, C, in English inches, the capillary elevation.

Change in form of the surface of liquids by others.

	A.	B.	C.	A.	B.	C.	A.	B.	C.
Chloroform . .	1·493	0·014	0·8	1·493	0·026	0·46	1·493	0·010	1·07
Hydrochloric acid	1·165	„	2·7	1·167	„	1·51	1·167	„	3·73
Solution of potassa	1·343	„	2·9	1·105	„	1·77	1·105	„	4·61

Capillary Depression of Mercury.—Frankenheim(1), with the aid of the syphon-shaped tubes above described, has also examined the capillary depression of mercury with reference to changes of temperature. He finds that the difference in height of both mercury levels increases as the thermometer rises, and it would appear proportional to the temperature. If the depression at the temperature t be

$$H = h\ (1 + a\ t)$$

h representing the capillary depression at the starting temperature, the constant coefficient *a* expressing the influence of heat will fall according to Frankenheim, between 0·0013 and 0·0014. The coefficient for the expansion of mercury is known to be 0·00018. Hence, the difference in height produced by the capillary force, progresses much more rapidly than the expansion of the mercury increases, or what is the same, than its density diminishes.

The depression of mercury in capillary tubes, is known to be due to the cohesion of the particles of mercury being greater than twice their adhesion for glass (Biot, Traité, 1, 448). Frankenheim attributes the depression of the mercury, increasing with the rise of temperature, to a simultaneous diminution of the cohesion of the mercury and of its adhesion to the sides of the tubes. If this explanation be correct, the adhesion ought to diminish more rapidly than the cohesion, in such a manner, that the latter would tend to preponderate. Exact measurements of the top of the mercury column, at various temperatures, can alone decide this question.

For calculating the capillary depression, Frankenheim gives the equation $H^{mm} = 4{\cdot}0 + 0{\cdot}0053t$, which holds good however for very dry glass only, or, at the ordinary state of the atmosphere, for higher temperatures, because at lower temperatures the adhesion of the glass (and with it the capillary depression) is lessened by the moisture with which it is covered.

(1) Pogg. Ann. LXXV, 229.

Capillary depression of mercury.

Thus, according to the above formula, we find at 0°, H = 4. It is found, however, actually to be 4·50.—

The estimation of the capacity of glass vessels, which are either partly filled with, or closed by mercury, is rendered difficult by the inflection of the mercury towards the sides of the vessel.

To ascertain the exact capacity, a knowledge is required of the position of a plane between the highest and lowest point of the meniscus, in such a manner that the fluid above exactly fills up the empty space below. Danger(1) has employed the following method for finding out the position of this plane. Cylindrical tubes, varying in width, and ground level at the top, were filled with mercury, and the excess carefully removed by means of a flat piece of plate-glass, made to slide across. On taking off the plate, with the precaution that no mercury was spilt, a meniscus was formed by the liquid separating from the sides, and rising in the centre. The ground glass rim is, in this case, the plane which is sought. Both the depression of the contact-line of the mercury below, and the elevation of its top above the rim, were measured by means of an appropriate telescope, provided with a micrometer-screw. The following table contains an abstract of the results, A representing in millimetres the interior diameter of the tube, B the elevation of the top of the meniscus above, C the depression of the base of the meniscus below the rim of the glass, and D the total height of the meniscus. They hold good for a temperature of 15° C. It is to be regretted that the author has omitted to notice the atmospheric conditions, under which his experiments were conducted, that is, whether they were made with a moist, dry, or ordinary atmosphere, as it is well known that the height of the meniscus is by no means independent of these influences.

A.	B.	C.	D.	A.	B.	C.	D.	A.	B.	C.	D.
1	0·178	0·143	0·321	10	0·643	0·900	1·543	28	0·380	1·302	1·682
2	0·310	0·261	0·571	12	0·637	0·988	1·625	30	0·355	1·325	1·670
3	0·410	0·369	0·779	14	0·610	1·056	1·666	35	0·297	1·375	1·676
4	0·486	0·467	0·953	16	0·570	1·110	1·680	40	0·248	1·415	1·663
5	0·544	0·558	1·102	18	0·530	1·157	1·687	45	0·208	1·450	1·658
6	0·584	0·643	1·218	20	0·495	1·190	1·685	50	0·187	1·480	1·667
7	0·610	0·710	1·320	22	0·455	1·224	1·679	55	0·180	1·511	1·691
8	0·630	0·782	1·412	24	0·436	1·252	1·688	60	0·178	1·540	1·718
9	0·639	0·844	1·483	26	0·408	1·278	1·686				

(1) Compt. Rend. XXVII, 381; Ann. Ch. Phys. [3] XXIV, 501; Pogg. LXXVI, 297.

Endosmosis.—It is well known, that the attention of physicists to the phenomena of endosmosis, has been attracted chiefly by the observation that two liquids separated by a porous diaphragm, impenetrable at small hydrostatic pressures, will usually pass to each other in unequal quantities. This was certainly a startling fact, inasmuch as the mutual attraction of two liquids, which is the cause of their passing the diaphragm, must evidently be equal on both sides; and physicists have consequently examined, with much eagerness, the proportion in which various liquids pass to each other. The instrument most frequently used for this purpose, is Dutrochet's *endosmometer*, which consists of a narrow glass tube, the lower extremity of which, widening in shape of a funnel, is closed with a bladder; this tube partially filled with the one, usually the heavier, is introduced into the other liquid. This apparatus, however, does not admit of the differences of level, at the various periods of the experiment, being measured with perfect accuracy, since every variation of the hydrostatic pressure in the endosmometer-tube, involves at once a change in the turgescence of the bladder. To avoid this inconvenience, Vierordt(1) has devised another disposition of the apparatus, which enables him to keep the pressure on both sides of the membrane perfectly equal, without interfering in the slightest degree with the changes gradually affecting the difference of level of the two liquids. He accomplishes this object by proportionally increasing the atmospheric pressure exerted upon the surface of the liquid, the volume of which is diminishing, by means of a very ingenious arrangement, pointed out to him by Eisenlohr, which indicates at once the slightest disturbance in the equilibrium of both liquids. Further details are unintelligible without the assistance of drawings.

Endosmosis.

Vierordt has examined, by means of this apparatus, the endosmosis of water, with regard to solutions of sugar and sea-salt of different degrees of concentration. It is evident from his investigation, that for an equal duration of the experiments, the difference of the velocities exhibited by the currents proceeding in opposite directions actually increases, with the amount of substance originally dissolved in a given volume of water, without however being accurately proportional to it, as Dutrochet had asserted. In all experiments, the proportion in which the volumes increase, was found to be smaller than that of the original densities.

(1) Pogg. Ann. LXXIII, 519; abstracted from Griesinger's Archiv. für Physiologische Heilkunde.

Endosmosis.

Jolly(1), in ascertaining the endosmosis of various saline solutions with water, has availed himself of a method different from the endosmometric procedure hitherto followed. He introduced the solution to be examined into an open glass tube, one end of which was closed by bladder, and ascertained the gradually ensuing changes of quantity by weighing; the external liquid, the water, being frequently changed, was kept as uniform as possible, until the weight of the tube was no longer affected, except by evaporation. The tube now contained distilled water, the dissolved matter having been entirely eliminated. The influence of evaporation was ascertained by means of a check tube, partly filled with water.

Jolly found in this manner, that certain quantities of soluble substances, whether dry or in solution, when passing into water, the temperature remaining unaltered, are replaced by proportional quantities of the fluid, which he calls *endosmotic equivalents*; at a temperature near 0°, sea-salt, *e. g.* was replaced by from 4·3—4·6 times, Glauber's-salt, by from 11—12 times its weight of pure water. This proportional amount of water, or the endosmotic equivalent, is however dependent upon the temperature, with which it increases.—Among various liquids, examined for the most part at low temperatures, potassa-solution required by far the largest amount of replacing water, more than 200 times the weight of the alkali; the endosmotic equivalent of neutral sulphate of potassa was found to be 12, that of the acid salt 2·3, that of hydrated sulphuric acid only 0·35.

The knowledge of the endosmotic equivalent of a substance, enables us to calculate the weight eliminated by a certain observed amount of replacing water, quite independently of the quantity originally dissolved, or of the concentration of the solution.

With the aid of his endosmotic equivalents, Jolly has also calculated the time requisite for the passage of certain quantities of soluble substances, *e. g.* of Glauber's-salt, through a membrane of a certain size, into water. For this purpose, the additional hypothesis was necessary, *that the amount of substance passing in the unit of time, was, cæteris paribus, proportional to the density of the solution.* The close coincidence of the calculated spaces of time, with those observed in experiment, removed any doubt that might have remained respecting the correctness of the above supposition.

Dutrochet's assumption that, for an equal duration of the

(1) Henle and Pfeufer's Zeitschr. für rationelle Medicin, VII, 83; in abstract, Ann. Ch. Pharm. LXVIII. 1.

experiment, the intensity of the endosmosis was proportional to the original density of the solution, already pointed out by Vierordt as erroneous, is, moreover, proved to be incorrect by Jolly's results. Calculation, as well as Vierordt's experiments, shows that the amount of water passing, is somewhat larger in the case of lower densities. Endosmosis.

It would be very important to confirm, by a more extensive series of experiments, the two laws resulting from Jolly's researches; viz., firstly, that the amount of salt permeating the membrane in the unit of time, is proportional to the density of the solution; and secondly, that, quite independently of this density, the quantity of salt eliminated in a certain time is replaced by the passage of an endosmotically proportional amount of water. Such a confirmation, when more general, would be an important support of the view,—that from the saline solution, salt-molecules only pass into the water, whilst the latter sends particles of pure water only into the salt solution.

Jolly explains, in a peculiar manner of his own, the unequal faculty exhibited by two liquids, of passing to each other, when separated by a porous diaphragm. It is based upon the hypothesis, that the porous substance simultaneously absorbs the two liquids, although in unequal proportions, according to its relative faculty of absorption. In this general form, however, the assumption is in opposition to various results of experience. Blotting paper, f. i. is wetted both by water and by oil. But when once soaked with water, it is perfectly impervious to the passage of oil, even under considerable pressure; whilst the latter is easily displaced from the pores of the paper by the former. It is evident that a porous substance is capable of simultaneously absorbing two liquids, only when they are miscible with each other; in other words, when they are endowed with a powerful mutual attraction; in this case, however, we do not require an hypothesis, not demonstrable by experiment, in order to comprehend the passage of two liquids through a porous diaphragm, even if no attraction were exerted upon one of them by the porous body. The absorption of two liquids ensues unequally, because one of them is acted on by two forces, namely, by the difference of the unequal adhesion of the two liquids to the diaphragm, and by the chemical attraction, whilst the other enters the pores under the influence of the latter force only. A gradual mixture of the two liquids would take place also without the presence of a membrane; the introduction however of a diaphragm, when endowed with a different degree of adhesion for both, must evidently alter the relation, in which the mixture proceeds. A salt-solution and pure water

Endosmosis. being separated by a piece of bladder, for instance, the former will receive more particles of water than the latter will particles of salt; the tendency to mix, exhibited by the two liquids, is due to two forces, opposite, but exactly equal; the adhesion, however, on both sides, is unequal. Accordingly, a volume of water, passing through the bladder into the salt-solution, cannot be replaced by an equal bulk of salt-water, since, the active force being unequal, the water moves with greater velocity. The whole question now turns upon the argument, that two liquids, unequally permeating a porous substance, actually exhibit an unequal adhesion to this substance.

For this purpose, Liebig(1) has examined the absorptive power of animal membrane in relation to pure water, solution of sea-salt, spirits of wine, and oil of marrow. He found that 100 parts, by weight, of dry ox bladder absorbed in 24 hours:

Pure water	268 vol.
Sea-salt solution, brine (1·204 spec. grav.) .	133 „
Spirits of wine of 84 per cent	38 „
Oil of marrow	17 „

100 parts, by weight, of ox-bladder, absorbed in 48 hours:

Pure water						. . . .	310	parts by weight.
Of a	mixture of	$\frac{1}{3}$	water,	and	$\frac{2}{3}$	sea-salt solution	219	„
„	„	$\frac{1}{2}$	„	„	$\frac{1}{2}$	„ „	235	„
„	„	$\frac{2}{3}$	„	„	$\frac{1}{3}$	„ „	288	„
„	„	$\frac{1}{2}$	alcohol	and	$\frac{1}{2}$	water	60	„
„	„	$\frac{1}{3}$	„	„	$\frac{2}{3}$	„	181	„
„	„	$\frac{1}{4}$	„	„	$\frac{3}{4}$	„	290	„

100 parts, by weight, of dry pig's bladder absorbed in 24 hours:

Pure water	356 vol.
Saturated solution of sea-salt . .	159 „
Oil of marrow	14 „

Now, if we consider that animal membrane possesses a very appreciable elastic force, which opposes the turgescence attending the imbibition of a liquid, we are justified in concluding that the cause of the absorptive power, *i. e.* the adhesion of the membrane to the liquid is proportional to the quantity absorbed. He found, indeed, that animal membrane, saturated with water, shrinks by the preponderance of the elastic force, as soon as this water is converted on addition of alcohol into a mixture of inferior penetrative power, and loses a portion of its former contents.

(1) Researches on the Motion of the Juices in the Animal Body, edited by Gregory; London, Taylor, Walton and Maberly.

On covering with pure water a piece of bladder saturated with oil, the latter is expelled and replaced by the same amount of water, which would have been absorbed without the previous introduction of oil. Endosmosis.

If a bladder, previously soaked in brine, be covered with pure water, the brine appears in drops on the other side, and every particle of salt would probably soon be expelled, just as in a former case, the oil, the pores of the membrane becoming filled with pure water; unless an additional force was exerted in this case, by the faculty which belongs to these two liquids of mixing with each other; under the influence of this new force, a portion of the salt moves in the direction of the water. A necessary consequence of this deportment is, that a membrane, when placed as a diaphragm between water and brine, must take up a mixture of both, in which, however, while the mixing proceeds in both directions, the proportion of water must always predominate. How much the process of endosmosis depends on the relation of the porous diaphragm to the separated liquids, is strikingly exhibited by the well known phenomenon, that alcohol, mobile as it is, passes through the membrane into water, in much smaller proportion than the latter liquid into alcohol. The reverse takes place if a thin sheet of collodion is selected as the diaphragm (Liebig).

The unequal attractive force, exerted by the material of the animal tissues, when separating various liquids, acts, as it were, like mechanical pressure, which is stronger from one side than from the other(1).

If a bent glass tube, whose shorter limb is closed with bladder after having been partially filled with brine, be introduced into pure water, the bladder being below the level of the liquid, we find, on introducing mercury into the longer limb, that at a certain height of the latter, the mixture of the two fluids will take place without change of volume. The action of the bladder, preponderating in one direction, is balanced by the pressure of the mercurial column, under whose influence the amount of brine displaced becomes equal to the quantity of water which enters. This experiment also refutes the view, still widely prevailing, that animal membrane being, when dry, almost impenetrable to atmospheric pressure, is, when moistened, incapable of transmitting hydrostatic pressure through its capillary pores. Liebig has endeavoured to measure directly the force requisite for pressing various liquids through the pores of animal membranes; he finds, that generally this force diminishes

(1) Researches on the Motion of the Juices, &c., 51.

Endosmosis. in proportion to the increased facility, exhibited by the porous substance, of swelling up, when absorbing a liquid. This force bears no relation to the degree of fluidity.

Thus water passes an ox bladder of $\frac{1}{10}$th of a line in thickness, when, under the pressure of 12 inches, a saturated sea-salt solution at from 18—20 inches, and oil (of marrow) at 34 inches. A pressure of 36 inches was not capable of effecting the passage of alcohol.

When the membrane used is the peritoneum of the ox $\frac{1}{20}$th of a line in thickness, water is forced through it by from 8 to 10 inches, brine by 12—16 inches, oil by 22 to 24 inches, and alcohol by 36—40 inches of mercury.

This pressure, however, does not remain constant; if the experiments are continued for any length of time, it in fact diminishes; the membrane, by long contact with water, evidently undergoing a change in consequence of which the pores become widened.

If a space filled with water be closed by bladder, one side of which is kept wet, whilst the other is surrounded by the atmosphere, the moisture will evaporate at the outer surface, being, however, continually replaced by water passing from the inner portion through the membrane. The liquid thus acquires a motion towards the evaporating surface, it gradually diminishes in quantity and in the same proportion the external pressure on the walls of the vessel is increased; fluids brought into contact with the outer surface of the bladder, *e. g.*, water, aqueous solutions, oils, spirits of wine, &c., may be forced by this pressure into the interior of the space, and this passage takes place even through several layers of bladder. Liebig(1), who illustrates this deportment by numerous instructive experiments, arrives at the conclusion, that the cutaneous transpiration, and the evaporation taking place at the surface of the lungs, must necessarily establish a similar motion of the juices in the animal body, namely, a motion towards the evaporating surface. He mentions the almost forgotten, but highly remarkable observations on the motion of the sap in plants, made more than 120 years ago by Stephen Hales, from which he inferred, even at that period, that it is the evaporation from the branches, leaves, flowers, and fruits, which causes not only the absorption of the water in the roots, but likewise its ascent to the top of the highest tree(2).

(1) Researches on the motion of the Juices, &c., (Comp. p. 71).
(2) Ibid. 77.

ATOMOLOGY.

Crystallization. New method of obtaining crystals in the dry way.

Crystallization. New Method of obtaining Crystals in the dry Way.—Ebelmen(1) has described a new method of obtaining various compounds in a crystallized state, by which minerals may be artificially imitated. He employs a substance capable, under the influence of a powerful heat, of dissolving the constituents of the compound to be prepared, and itself volatile at this temperature, so that the compound separates on the evaporation of the solvent. Such substances are boracic acid and borax. By continuously heating in the porcelain furnaces of Sèvres a mixture of alumina and magnesia with fused boracic acid, he obtained, on cooling, a mass interspiculated with small crystals, possessing both the physical properties and the chemical composition of spinel ($MgO, Al_2 O_3$), and to which a pink, blue or black colour could be imparted by the addition to the ingredients of sesquioxide of chromium, protoxide of cobalt, or sesquioxide of iron. Exactly in the same manner, and of the same crystalline form (regular octohedron) he prepared the compounds of alumina with the protoxides of manganese, of iron and cobalt, and with lime; those of sesquioxide of chromium and alumina, with protoxide of iron and magnesia; of the sesquioxides of chromium and iron with protoxide of iron; and lastly, those of sesquioxide of chromium with magnesia, and with protoxide of manganese. In the same manner microscopic crystals of cymophane (chrysoberyl, aluminate of berylla, $BeO, Al_2 O_3$) were artificially obtained; and also a crystalline compound of alumina with baryta. Sesquioxide of chromium, when mixed with carbonate of lime and fused boracic acid, and exposed persistently to a powerful heat, crystallized. Emerald likewise was found to be soluble in boracic acid, from which it separated in the crystalline state, and peridote (chrysolite) was formed artificially with all the properties of the mineral. Instead of boracic acid, borax was successfully used for crystallizing alumina with the properties of corundum.

Formation of Crystals.—Knop(2) has communicated observations on the formation of crystals, especially respecting their distortion, aggregation, striation, &c., in the case of alum. We refer to the paper, the details being unintelligible without the aid of drawings.

Crystallography.—New views on crystallization and crystallo-

(1) Ann. Ch. Phys. [3] XXII, 211; J. Pr. Ch. XLIII, 472; in abstract Compt. Rend. XXV, 279, 661; Ann. Ch. Pharm. LXVIII, 261; Phil. Mag. [3] XXXI, 311; XXXII, 312.

(2) J. Pr. Chem. XL. 90; XLI, 81.

Crystallography.

graphy, have been communicated by Leeson(1). He finds that the methods of classification now in use (there is, however, only one method generally acknowledged by the crystallographers of the present time) are, in many instances, imperfect and obscure, and that the nomenclature is more or less confused and inappropriate. The difficulties encountered in 1808 by Bournon, when engaged in determining various modifications of crystals of the same substance, are again attacked by Leeson, and in his endeavours to remove them he has not availed himself of the labours of German crystallographers in the same field. Leeson follows a method, by means of which he points out numerous errors committed in the determinations made up to the present moment;—(in fact, apophyllite had never been determined as crystallizing in rhombic dodecahedrons; the six-sided prism, terminating pyramidally, had not yet been considered as a simple form; calc-spar had not been observed in forms closely approximating those of fluor-spar and galena; garnet, analcime, and calc-spar, had not been adduced as arguments for the occurrence of the same form, &c.). Our space will not admit of following the author through his memoir in further detail.

In the magnetic iron of Achmatow, according to Kokscharow(2), the hexakisoctohedron $\frac{7}{5}$ O $\frac{1}{3}$, is met with in subordinate combination.

Dana(3) has published a paper on the laws of cohesion. He inclines to the view, that the passage of inorganic bodies from the liquid into the solid state, is invariably attended with the assumption of crystalline structure. His notion is, that the smallest spherical or spheroidal particles of bodies are endowed with particular lines (axes), to which attraction is principally exerted, and the terminations of which exhibit a difference of polarity. In more fully developing this view, he endeavours to deduce the crystallographical and crystallophysical properties of bodies. For details, we refer to the original, as speculative investigations of this kind do not admit of a short abstract. In a special consideration of the crystallization of snow, Dana(4) has given a more detailed illustration of his views.

Hemihedrism.—The crystallographical law, that corresponding parts of a crystalline form are uniformly altered by combination, suffers an exception whenever the form combining with the fundamental one is

(1) Chem. Soc. Mem. III, 486—560.
(2) Pogg. Ann. LXXIII, 188.
(3) Sill. Am. J. [2] IV, 364.
(4) Ibid. [2] V, 100.

hemihedric. Rivière(1) contests this exception, which, in his opinion, is only apparent; he asserts (on observations made with sulphate of magnesia and with boracite) that in corresponding parts of the fundamental form, the same planes of combination invariably occur, but that some of them are so minute as to be invisible without a lens, and frequently even with its assistance. It is difficult to conceive, how these observations oppose the doctrine of hemihedrism, and how they can be considered as an argument, that Hauy's law of symmetry holds good in *all* cases. Even if all the corners of a cube of boracite are truncated, the truncation, as is well known, is by no means uniform, inasmuch as the planes of the one tetrahedron exhibit a physical deportment different from those of the other. Hemihedrism.

Teratology of Crystals.—Holger announced in 1837, that he intended to enrich mineralogy by the pathology of minerals, *i.e.*, by the investigation of the question, how far minerals may be diseased in composition, form, or origin. Part of this scientific field has been selected for cultivation by Baudrimont(2), who communicates researches on the *Teratology* (doctrine of monstrosities) of crystals, commencing with observations on calc-spar. He has examined its cleavage, which, for the most part, was found to be different in crystallographically equivalent directions; he has likewise investigated the lustre, &c., of the planes, and the angles formed by the terminal edges in one and the same crystal (the principal rhombohedron). The influence of geminal formation is not considered.

Difference of Angles in Crystals.—In a note on the causes of the angular differences in artificial crystals, Nicklès(3) attributes the discrepancies (sometimes exceeding a degree), occurring in his measurements of different crystals of bimalate of ammonia, to the presence of impurities not appreciable by analysis.

Microcrystallometry.—An instrument for the determination of microscopic crystals, by measuring their angles, has been described by Frankenheim(4). The moveable eye-piece of the microscope is furnished with a graduated circle, the body with a vernier, cross wires being placed in the focus of the eye-piece. The apex of the angle to be measured being placed in the centre of the cross, and one of its limbs being covered by one of the wires, the eye-piece is turned until the other limb appears under the same wire, when the amount of the rotation is read off. Frankenheim has not recorded any accurate determinations made by means of

(1) Compt. Rend. XXV, 638.
(2) Ibid. 668.
(3) Ibid. XXVII, 270; J. Pr. Chem. XLV, 372
(4) Pogg. Ann. XXXVII, 637.

Microcrystallometry.

this instrument; nor have any such results been published by Chevalier(1), who proposed two glass plates rotating upon each other, each having a diameter ruled with the diamond, which is made to coincide with one of the limbs of the crystal-angle to be measured. Pacini(2), likewise, who proposed to turn the object, the stage of the microscope being provided with a rotating graduated circle, mentions no determinations made according to his plan.

C. Schmidt(3) has carefully investigated a series of crystalline substances according to Frankenheim's method, which he has minutely examined as to sources of error, &c. By these observations the applicability of this method is established beyond any doubt. Interesting in this respect, is a comparison given by Schmidt(4), of his results obtained in microscopically measuring the crystals of phosphate of magnesia and ammonia, with those of Teschemacher, who, working with larger crystals of the same compound, as found in guano (Teschemacher's guanite, identical with Ulex's struvite) availed himself of the reflecting goniometer. This compound belongs to the rhombic system. The ratio of brachydiagonal, microdiagonal, and principal axis, was found to be:

0·5141 : 1 : 0·6241 by Schmidt.
0·5429 : 1 : 0·6233 by Teschemacher.

More complicated for ordinary measurements, is an arrangement described by Leeson(5), who proposes to substitute for the cross wires a doubly refracting prism, of such dimensions that the two images of the object obtained therewith, are not perfectly separated from each other. A plane angle of a crystal is measured under the microscope, by revolving the tube containing the prism until both images coincide, first in the direction of the one, and then in that of the other side of the crystal; the amount of rotation gives the angular distance.

Goniometer.—Matthiesen(6) has described an instrument to be used both as a mechanical, and as a reflecting goniometer.

Connection between Composition and crystalline Form.—Researches on the most recondite causes of crystalline form have been communicated to the Academy of Paris by Gaudin(7). He confines his

(1) Des Microscopes et de leur usage, etc.; Paris, 1839.
(2) Nuovi Annali delle Scienze Naturali di Bologna, 1845, Novembre.
(3) Krystallonomische Untersuchungen, oder Entwurf einer allgemeinen Untersuchungsmethode der Säfte und Excrete im thierischen Organismus. Mitau u. Leipz. 1846.
(4) Ann. Ch. Pharm. LXI, 323.
(5) Chem. Soc. Mem. III, 550.
(6) Compt. Rend. XXIV, 781.
(7) Ibid. XXV, 664.

communication to the consideration of examples of six-planed and twelve-planed bipyramidal molecules, and of the three forms derived therefrom, namely, the rhombohedron, right and oblique rhombic prism. According to Gaudin, the form of a crystal is determined by the number and nature of its atoms; 3 atoms A form an equilateral triangular base, 2 atoms B an axis crossing it; 3 A 2 B, therefore, *"une double pyramide trièdre, c'est-à-dire un hexaèdre; alumine, sesquioxyde de fer."* The common expressions of crystallographical nomenclature appear to be used in this paper in a peculiar sense. Nitre, as to its crystalline form, (Gaudin, certainly did not think of Frankenheim's statement) appears side-by-side with calc-spar, and with quartz; felspar too, would crystallize in rhombohedrons, if pure; but it contains water and an excess of silica, and has an axis 7 atoms in length, which will not admit of its crystallizing as a right rhombic prism. If the reader should not understand these specimens of Gaudin's theory, he must patiently wait until the publication of the whole of the system, to which Gaudin refers *"afin d'être mieux compris."*

Connection between composition and crystalline form.

The connection of crystalline form and chemical composition has been likewise investigated by Delafosse(1); his researches also have been communicated only in abstract. According to his opinion the components of a chemical compound constitute partly the nucleus and partly the shell of a crystalline molecule, whose form is determined by the number of atoms composing both the nucleus and the shell. In the regular system, simple (holohedric) forms occur, of 6, 8, 12, 24 and 48 planes; alum, crystallizing in the regular system, contains 24 atoms of water which are shell-atoms, each of them corresponding to a plane of the crystalline molecule. In the case of substances which also exhibit tetrahedric planes, we find the number of the supposed shell-atoms suddenly compared with the number of planes, not of a simple form, but of a combination; in this case 4 had to be added to the above numbers. In a similar manner Delafosse conceives the form of square-prismatic and of hexagonal crystals, and promises, in a continuation of his investigation, to apply the knowledge thus acquired to the exposition of the siliceous minerals; this application, however, was possible only by adopting Si O as the formula of silicic acid, and by no longer representing the silicates, as had been frequently done, as double compounds, *i. e.* by no longer arranging silicic acid with alumina and the other bases (of the formula Me O of course). This conclusion, and the

(1) Compt. Rend. XXVI, 90.

Connection between composition and crystalline form.

acquaintance with an octohedric borax crystallizing with 5 eq. of water, form sufficient data for a proper estimation of Delafosse's views. Moreover, the fundamental principle of these views has been claimed by Baudrimont(1), who does not, however, agree with its elaboration by Delafosse; his reclamation of priority has been answered by Delafosse(2).

Laurent, by applying some peculiar views of his own, endeavours to explain the differences presented in the analyses of substances, which, on the ground of their physical properties, and especially of their crystalline form are considered as belonging to the same species, (epidote, for instance). By the same views he tries to remove the anomaly of similar crystalline forms occurring with oxides and sulphides, which, according to opinions pretty generally adopted, are represented by different chemical formulæ. Laurent(3) believes that the oxides of the formula $Me_2 O_3$ likewise contain an equal number of atoms of both constituents, and are capable of replacing, in varying proportions, and without change in the crystalline form, the other oxides of the composition (Me O). He assumes, for instance, for sesquioxide of iron, a composition similar to that of the protoxide; in his opinion sesquioxide of iron contains 1 atom of oxygen and 1 atom of an iron, with an atomic weight different from that of the iron in the protoxide. In a similar manner he proceeds with the sulphides.

Pasteur(4) has instituted researches on the connection between chemical composition, crystalline form, and direction of circular polarization. He points out that, in all tartrates (neutral, acid and double salts) planes of approximately the same inclination are observed; all tartrates exhibited a similar construction in *one* part, and it was only about the boundaries of this part that different planes and different terminations generally occurred. The racemates resemble, in this respect, the tartrates. It appears that the prismatic nucleus of the crystalline molecule in all these salts is formed by the proximate constituent of invariable composition, while the varying quantities of base, or water of crystallization, accumulated towards the end of the molecule, give rise to dissimilar formation. Pasteur then points out the occurrence of hemihedric formation in tartrates; he states that hemihedrism might be exhibited sometimes by the one, sometimes by the other of the homologous terminating planes, so

(1) Compt. Rend. XXVI, 209.
(2) Ibid. 335.
(3) Ibid. XXVII, 134; Pharm Centr. 1848, 679.
(4) Ann. Ch. Phys. [3] XXIV, 442; the abstract, Compt. Rend. XXVI, 535; Inst. 1848, 157, is completed by the report of Regnault, Balard, Dumas, and Biot, Compt. Rend. XXVII, 101; Instit. 1848, 331.

that hemihedrically-formed crystals of the one kind presented a catoptric image of those of the other; he distinguishes both kinds as right and left hemihedrism. With tartrates only one kind of hemihedrism occurred, and all of them, when in solution, turned the plane of polarization in the same direction. Of the various crystals deposited from a solution of the common racemate of soda and ammonia, (which, according to Mitscherlich, does not turn the plane of polarization), some exhibited right, and others left hemihedrism; the two kinds of crystals, collected, separated, and dissolved, turned the plane of polarization, the former in the one, the latter in the other direction. These two kinds of crystals yielded, by treatment with soda, a simple soda-salt, turning the plane of polarization, either to the right or to the left hand, in perfect accordance with the direction imparted by the double salt used in its preparation; the acid separated from one or the other of the double salts was likewise endowed with a rotating power in the one or the other direction. The common racemic acid of chemists, (which does not turn the plane of polarization,) hence contained two acids of opposite rotating power, one of which was most likely tartaric acid. Pasteur thinks it probable that all substances producing circular polarization are hemihedric; in sugar this is certainly the case.

Connection between composition and crystalline form.

The researches of Pasteur afforded an opportunity to Laurent(1) of reminding us of some views proposed by him at an earlier period, and which did not obtain the approbation of inquirers. He is positive on the following points: 1. That a body might possess two distinct, but similar forms, and that a transition from one into the other could take place under trifling influences; 2. That two different substances of analogous composition could be isomorphous, even when belonging to different systems of crystallization, *i. e.* a cube could be isomorphous with a rhombohedron, the edges of which form an angle of nearly 90°, an hexagonal prism with a rhombic prism of an edge-angle of nearly 120°; 3. That bodies belonging to the same series of chemical compounds, but not presenting an analogous composition, (not exhibiting in their formulæ the same number of elementary atoms,) could be either entirely or partially isomorphous or hemimorphous. Substances similarly shaped in *one*, dissimilarly shaped in other directions, are, according to Laurent, hemimorphous.

Assertion 1) is stated to be confirmed by Pasteur's observations; we shall consider them below (p. 25). Assertion 2) is true only if we limit ourselves to an approximate consideration both of the form

(1) Compt. Rend. XXVI. 632; J. Pharm. [3] XIV, 209.

Connection between composition and crystalline form.

and angles of a crystal, the consideration of the question, to which law of symmetry a form is to be referred, *i. e.* of the system of crystallization to which it belongs, being altogether neglected; in the case instanced by Laurent, of a cubic substance A being isomorphous with the rhombohedric B, most crystallographers would more correctly state, the substance A crystallized as a rhombohedron, the edges of which happened to agree closely with 90°.—Assertion 3), finally is stated to be confirmed by Pasteur's observations on the tartrates (p. 22). All depends here on the conception of the term isomorphism; the original meaning being that of equal or similar form with analogous composition; Laurent's appears to be that of equal or similar form with a somewhat similar composition (*e. g.* the presence of the same acid in several salts); the latter conception is extremely vague. As an additional support of the correctness of assertion 3), Laurent adduces, moreover, that acetate and butyrate of copper exhibit the same crystalline form (with the latter only the combination ∞ P . o P of the monoclinometric system was observed), notwithstanding that the former salt contains 1 equivalent, the latter 2 equivalents of water of crystallization. According to Lies(1), however, the latter salt also contains only 1 equivalent of water of crystallization.

In conclusion, Laurent mentions that an analogy of composition might be constructed for the concordant form of calc-spar and nitrate of soda (a possibility already pointed out by Schaffgotsch(2), and that for the formulæ $N\,Na\,O_6$ and $C_2\,Ca_2\,O_6$, the specific volumes of both salts are found to be nearly the same (an accordance already pointed out by H. Kopp(3).

Nicklès(4) also has mentioned some instances in which the similarity of components is manifested in a similar elaboration of form at *one* part, whilst the diversity of constituents is exhibited in a dissimilar elaboration beyond this part. He considers formiate of baryta (anhydrous), acetate of baryta (which contains 3 equivalents of water), and metacetate of baryta (which contains 1 equivalent of water) as hemimorphous, in Laurent's acceptation of the term; it is true, the crystals of the former salt are rhombic, those of the two other salts monoclinometric; in all three, however, we find prismal planes, exhibiting an inclination under nearly the same angle. Nicklès' statements respecting the acetate with 3 equivalents of water, differ however from those of Brooke. The similarity

(1) Compt. Rend. XXVII, 321.
(2) Pogg. Ann. XLVIII, 335.
(3) Pogg. Ann. LIII, 458.
(4) Compt. Rend. XXVII, 611; Instit. 1848, 390.

of composition refers in this case to the acids belonging to *one* series. Chlorate and perchlorate of potassa, likewise, according to Nicklès, are hemimorphous; these two salts, also, crystallize in two different systems.

Connection between composition and crystalline form.

Dimorphism.—Several physicists have endeavoured to demonstrate a certain relation existing between essentially different forms, affected by the same chemical compound, or to reduce one to the other; long ago calcareous-spar and arragonite elicited such inquiries, and at a later period (1824) the rhombic and monoclinometric crystals of sulphur have been considered from a similar point of view by Kupffer(1). More recently, a more extensive series of dimorphous substances have been examined in this respect by Pasteur(2). He thinks that he is able to demonstrate that isomorphism is only an apparent anomaly in the laws of crystallization. In the various modifications of a dimorphous substance, the difference was more exhibited in the law of symmetry, than in the fundamental form; in all of them, fundamental forms might be traced, of dimensions closely concordant or bearing a simple relation to each other. He first endeavours to demonstrate this in the case of sulphur, whose monoclinometric crystals affect the form of a prism, the lateral planes of which are inclined at 90° 32′ and 89° 28′, whilst the angles formed by the lateral and terminal planes are 94° 6′ and 85° 54′; in the rectangular prism of the rhombic system, to which the other modification of sulphur belongs, all the angles are = 90°. Again, in both monoclinometric and rhombic sulphur, planes occur exhibiting nearly the same angle with the terminal planes. Pasteur considers the fundamental form in both modifications of sulphur to be nearly the same, the angles of inclination of certain planes being very similar, whether the crystallization of the sulphur was influenced by the law of symmetry of the rhombic or monoclinometric systems.—In a similar manner, Pasteur considers other dimorphous substances; several relations pointed out by him are very interesting, but neither a general law, nor even a confirmation of his view, can be deduced from his investigations. Angular differences, amounting to 3° or 4°, not being regarded in the fundamental forms of the different modifications, there is no form in any system which could not, on the law of the change of axes in simple relations, be made comparable with every other form within these

(1) Pogg. Ann. II, 423.

(2) Ann. Ch. Phys. [3] XXIII, 267; in abstract, Compt. Rend. XXVI, 353; J. Pharm. [3] XII, 453; Instit. 1848, 94.

Dimorphism. limits, particularly if forms are considered comparable, which are as dissimilar as an oblique rhombic prism, and a right rectangular prism (the latter being the same for all substances belonging to the rhombic system, and, consequently, not characteristic of any one). Pasteur's view, that dimorphism depends more upon the law of symmetry than on the dimensions of the fundamental form, is in strong opposition to the fact, that the different modifications of dimorphous substances may belong to the same system of crystallization. He endeavours indeed to remove this contradiction, by asserting that such modifications were not isomorphous, but isomeric; this, however, leads him to contradict his own theory, inasmuch as he starts with considering dimorphous substances generally as a class of isomeric bodies, and this confusion is by no means cleared by his afterwards pointing out that those substances are isomorphous in which the molecular arrangement is subject only to slight variations.—The arbitrary nature of Pasteur's comparisons is evinced, moreover, by the circumstance that Kupffer, (with whose investigations Pasteur appears to have been unacquainted), by comparing the two forms of sulphur in a perfectly different position, arrived nevertheless at a much closer concordance of the angles.—Pasteur's results are contradicted also by the following fact: sulphate of protoxide of nickel ($NiO, SO_3 + 7 HO$) occurs in square-prismatic and in rhombic crystals, in the latter case, in prisms nearly rectangular.—According to Pasteur, the section of these prisms, which is nearly square, corresponds to the square one of the other modification; he considers the principal axis of the square crystals to correspond with the principal axis of the rhombic modification. We should accordingly imagine that, in a rhombic crystal, when passing without change of its external outlines, into an aggregate of square crystals, the principal axis of the latter would be parallel with the principal axis of the former crystal. However, in effecting this passage slowly, the reverse may be very distinctly observed; the principal axis of the square form stands at a right angle to the principal axis of the rhombic form.—The introduction to Pasteur's investigations contains, moreover, the additional assertion, that it is intended to demonstrate the possibility of determining, *a priori*, which bodies are susceptible of dimorphism, and of fixing the general characters of the second form. This possibility is scarcely obvious from his researches.

Polymeric and heteromeric Isomorphism.—Respecting the views of Scheerer on polymeric isomorphism, and those of Hermann on heteromerism, both based upon examples exclusively borrowed from mineralogy, the reader is referred to our mineralogical Report.

Specific gravity. Determination of the specific gravity of solid bodies.

Specific Gravity. Determination of the specific Gravity of solid Bodies.—G. Rose(1) has communicated some experiments respecting the errors occurring in the determination of the specific gravity of solid bodies, when weighed in the state of finest division. His experiments embraced gold, silver, platinum, and sulphate of baryta. The specific gravity of gold, when fused alone, was found to be 19·30 to 19·34, when fused under carbonate of soda 19·32 to 19·33, under borax 19·33 to 19·34, under chloride of sodium 19·30 (the determinations refer to 17°·5). When compressed by a coining press, gold was found to have a specific gravity of 19·31 to 19·34. The specific gravity of finely divided gold, when precipitated by green vitriol, was found to be 19·55 to 20·72, and 19·49 when precipitated by oxalic acid. The specific gravity of silver was 10·53 when fused, 10·57 when compressed, 10·56 to 10·62 when precipitated, from the nitrate, by means of sulphate of protoxide of iron. Finely divided platinum, obtained by ignition of the binoxide, showed as high a specific gravity as 26·14, while that of the metal in the compact state is only 21 to 22. In later experiments, made with platinum black, prepared by various processes, the specific gravity was found to be between 16·63 and 22·89, once even only 14·89. In determining the specific gravity of the crystalline sulphate of baryta, as occurring in nature, Rose observed 4·48 to 4·49, while the specific gravity of the precipitate, as formed on addition of sulphuric acid to chloride of barium, was found to be 4·53. Rose concludes that substances, when finely divided, exhibit higher specific gravities than when occurring in compact masses, that the numbers obtained for the specific gravities increase with the minuteness of the division, and that these discrepancies arise from the condensation of water on the surface of the substances, augmenting with the degree of their division.

Osann(2) draws attention to some earlier experiments(3) made by him with platinum and glass. He had observed that the specific gravity of platinum diminished, whilst that of glass increased, when larger quantities of the substances were employed in the experiments; and he believes that this result is to be attributed to the attraction of water for, and consequent condensation of its vapour upon glass, whilst platinum (especially with a somewhat greasy surface) had an opposite tendency.

(1) Pogg. Ann. LXXIII, 1; LXXV, 403; in abstract Ann. Ch. Pharm. LXVIII, 159.
(2) Ibid. LXXIII, 605.
(3) Ibid. XI; Kastner's Arch. II, 58.

Specific gravity. Determination of the specific gravity of solid bodies

Grassi(1) communicates several specific gravities, which he determined with Regnault's volumenometer. His results are as follows:

Nitre in large crystals	2·109	Potato-flour	1·502
„ „ small crystals	2·143	Starch	1·529
„ fused . .	2·132	Oak-wood, dry	1·505
Sea-salt, dry .	2·142	Cotton	1·949
Rock-salt . .	2·207	Wool	1·614
Powder, for guns	2·085	Yarn	1·792
„ for muskets	2·189	Sponge	1·921

H. Rose has examined the changes of density occurring in alumina, and in niobic, pelopic, and tantalic acids, when exposed to different degrees of temperature. (See below, Report on these substances).

Determination of the specific Gravities of Liquids. Hydrometer.—Alexander(2) has proposed the application of a long-known principle for determining the specific gravity of liquids. Two parallel graduated glass tubes, both open at one end, and communicating with each other at their other ends, at which is a small syringe, are introduced, the one into water, the other into the liquid to be examined. The air in the tubes is now slightly rarified by means of the syringe, when, by comparing the elevation of the water, and of the other liquid in the tubes, the ratio of the specific gravities is given. Alexander calls this instrument *hydrometer*; he recommends it for practical purposes, but it is scarcely probable that it will be generally adopted.

Determination of the specific Gravity of Gases.—R. F. Marchand(3) has determined the specific gravity of several gases according to a new method. A large glass balloon is filled with a gas, which is then expelled by another gas, and fixed by proper absorbents, both temperature and pressure remaining constant during the experiment. The increase in weight of the absorbent, which of course must have no attraction for the replacing gas, indicates the amount of gas expelled. If the same balloon be employed in consecutive experiments with several gases, the weights of equal volumes are obtained, and hence the ratio of their specific gravities. In Marchand's experiments, oxygen for instance was displaced by carbonic acid, and absorbed by either copper or phosphorus; carbonic acid expelled by atmospheric air, was fixed by potassa, &c. The specific gravity of oxygen being 1, that of carbonic acid was found to be

(1) J. Pharm. [3] XI, 184.
(2) Pogg. Ann. LXX, 137; in abstract Ann. Ch. Pharm. LXIV, 153.
(3) J. Pr. Chem. XLIV, 38; Ann. Ch. Pharm. LXVIII, 202.

1·3825 and 1·3819, that of carbonic oxide 0·87563, that of sulphurous acid 2·04116, as the average results of a series of well concordant experiments. Determination of the specific gravity of gases.

Relation between Composition and specific Gravity. Of Gases.—Hunt(1) has communicated his views, why, in the gaseous state the specific gravity of sulphur is treble, and that of nitrogen only half of what the specific gravity of these bodies should be, if equivalent quantities of sulphur, nitrogen, and oxygen, (in the state of gas) occupied the same space. According to Hunt, the sulphur with which we are acquainted is S_3, and belongs to the same type as ozone (O_3), and sulphurous acid (SO_2). Elementary nitrogen is unknown; the gas obtained from atmospheric air by the removal of oxygen, being NN, an amide (most likely nitryle).

Specific Volume of solid Bodies.—Filhol(2) has published the first part of his researches on the relations existing between atomic weight, crystalline form, and specific gravity. His memoir contains some observations on the investigations in this field by others, (incompletely studied, as it appears, by Filhol), with determinations and views of his own.

No details are given as to the methods followed in determining the specific gravities; in some cases indications of these methods would have been very desirable. Filhol gives the following determinations:

IO_5	4·250	KI	3·056	KO, SO_3	2·625	KO, HO	2·044
AsO_3	3·884	NaI	3·450	NaO, SO_3	2·629	NaO, HO	2·130
AsO_5	4·250	BaI	4·917	SrO, SO_3	3·770	BaO, HO	4·495
		PbI	6·384	CaO, SO_3	3·102	SrO, HO	3·625
BaO	5·456	HgI	6·250	MgO, SO_3	2·628	BaO, 9 HO	1·656
SrO	4·611	AgI	5·500	ZnO, SO_3	3·400	SrO, 9 HO	1·396
CaO	3·180			CuO, SO_3	3·530	ZnO, HO	3·053
ZnO	5·612	KS	2·130	FeO, SO_3	2·841	CaO, HO	2·078
PbO	9·361	NaS	2·471	AgO, SO_3	5·410	BaCl + 2 HO	2·664
CuO	6·322	KO, CO_2	2·267	PbO, SO_3	6·300	SrCl + 6 HO	1·603
Al_2O_3	4·154	NaO, CO_2	2·509			CaCl + 6 HO	1·635
		BaO, CO_2	4·565	NaO, SO_3 + 10 HO	1·520	MgCl + 6 HO	1·558
KCl	1·994			CaO, SO_3 + 2 HO	2·331	FeCl + 4 HO	1·926
NaCl	2·240	NaO, NO_5	2·260	MgO, SO_3 + 7 HO	1·751		
BaCl	3·750	BaO, NO_5	3·200	FeO, SO_3 + 7 HO	1·904	SrO, NO_5 + 5 HO	2·113
SrCl	2·960	SrO, NO_5	2·857	ZnO, SO_3 + 7 HO	2·036	CaO, NO_5 + 4 HO	1·780
CaCl	2·240	CaO, NO_5	2·240	CuO, SO_3 + 5 HO	2·286	$NaO, 2 BO_3$	2·367
FeCl	2·528	PbO, NO_5	4·581	$Al_2O_3, 3 SO_3$ + 18 HO ?	1·569	$NaO, 2 BO_3$ + 10 HO	1·692

Filhol finds, that the specific volumes of baryta and strontia, when calculated according to the specific volumes admitted by H. Kopp

(1) Sill. Am. J. [2] VI, 170.
(2) Ann. Ch. Phys. [3] XXI, 415; in abstract Ann. Ch. Pharm. LXIV, 155.

Specific volume of solid bodies.

for barium, strontium and oxygen in a state of combination, accord with the results obtained by direct observation; he believes, but erroneously, that he has thus proved that barium and strontium enter into combinations under their original specific volume. In order to show that the specific volumes of the salts of heavy metals, in the oxides of which oxygen is assumed under the same specific volume, may be explained as well by the theory of oxygen-, as by that of hydrogen-acids (a fact, which nobody has ever doubted), he gives, with all the details of calculation, 31 empirical proofs of the mathematical truth, that $(A + B) + C = A + (B + C)$. Filhol returns to the methods, superseded by recent researches, of comparing the specific gravity of a chemical compound (D), the specific gravities of both of whose constituents are known, with that of a mixture of both constituents in the same proportions (Δ). He calls the value $\frac{D - \Delta}{D}$ the coefficient of condensation which was formerly expressed by $\frac{D}{\Delta}$, (whenever the coefficients of condensation under one acceptation of the term are found to be equal for several compounds, they are so, likewise, under the other acceptation). Like others before him, Filhol finds for analogous compounds the coefficients of condensation to be sometimes concordant, and sometimes very discrepant, and he observes, that the coefficients having been found to be the same for two compounds, the specific gravity of the one may be calculated ("*a priori*" as he calls it) by means of the coefficient of condensation ascertained for the other. He finds, however, also, and very justly, that the coefficients of condensation are not sufficiently concordant to found a general law upon this observation.

Specific Volumes of hydrated Salts.—A memoir on the specific volumes of hydrated salts, and their connection with the specific volumes of the constituents, has been published by Joule and Playfair(1). At an earlier period they had asserted, and endeavoured to confirm by observation, that, of salts containing a large quantity of water of crystallization, the constituent, present in solution along with the water, did not occupy any space, and that the hydrated salts in the solid state occupied the same space as the water contained therein, for the specific gravity of which, however, that of ice 0·9184, (or the specific volume 9·8, always referring to atomic weights of the hydrogen-scale $H = 1$), was to be assumed

(1) Chem. Soc. Qu. J. I, 139.

in some salts, in others 0·8163 (or the specific volume 11·025). The specific volumes were multiples of the number 1·225, which is adopted as the unit of volume, to which the other statements refer.

Specific volumes of hydrated salts.

Their assertions having been received with some doubts, the present memoir is intended to prove the correctness of their views in the case of some salts, and particularly that they contain the water with the volume of ice; however, this new line of argument also still admits of doubts.

They show, that the specific volumes of the salts $NaO, CO_2 + 10\ HO$; $2\ NaO, HO, PO_5 + 24\ HO$; $3\ NaO, PO_5 + 24\ HO$; $2\ NaO, HO, AsO_5 + 24\ HO$, and $3\ NaO, AsO_5 + 24\ HO$, as deduced from direct observation of the density, are almost accurately represented by values, which are obtained by multiplying the number of equivalents of water of crystallization by 9·8 (the specific volume of ice). They conclude, that in these cases, space was occupied only by the solid water, the other constituents occupying no space. The same is found with cane-sugar and milk-sugar; carbon, as filling space, had disappeared in these instances.

This (theoretically incomprehensible) result is not observed with other salts, for instance, with sulphates; with the hydrated sulphates of CaO, ZnO, MgO, FeO, NiO, NaO, Al_2O_3, with borax and pyrophosphate of soda, this annihilation as to space affects by no means all the constituents occurring along with the water, but only the acid. In these salts the base occupies the same space as when isolated, the water the same as when converted into ice; both fill the total volume of the salts, the acid only has ceased to occupy space. This theoretical speculation is also confirmed by the sulphate of protoxide of nickel, by assuming it, (as Joule and Playfair have done), to contain 6 equivalents of water, when calculation gives exactly the specific gravity found for the salt crystallizing with 7 equivalents of water, (which is isomorphous with the sulphate of protoxide of zinc); the latter determination is adduced as confirming the former calculation.

The same confirmation is derived from the alums, in which also the 4 equivalents of sulphuric acid fail to occupy space, the whole space being filled by the 24 equivalents of water of crystallization, (considered as ice), with the bases, (the specific volumes of which are, in some cases, assumed to be different from what has been found by direct observation; alumina, sesquioxide of iron, &c., being present in the alums in the unignited state).

A very different deportment is observed with the double salts, containing with 1 equivalent of sulphate of protoxide of zinc, or

Specific volumes of hydrated salts.

an isomorphous oxide, 1 equivalent of an alkaline sulphate, and 6 equivalents of water. In these salts the space is filled by the 6 equivalents of water, as ice, by the alkaline sulphate, and by the base of the other sulphate; the sulphuric acid of this latter salt has ceased to occupy space. It deserves to be remarked, that according to the numbers of Joule and Playfair, we may just as well assume that the sulphuric acid of the alkaline sulphate has lost the power of occupying space; both hypotheses lead to exactly the same results.

That the authors of this memoir are investigators of established reputation, does not remove the incomprehensibility of the proposition, that in phosphate of soda, which we have before our eyes, it is only the water which fills space, neither acid nor base occupying any. As if by magic, the latter, as relating to space, appear only on heating.—Acid and base occupy no space, *because* the assumption has been made, that the water is present with the specific volume of ice, whence no room is left for them.

It is very probable, that the concordant results obtained by Joule and Playfair, are due to some peculiar law; the expression, however, which they have chosen is inadmissible. They find this expression confirmed by the fact of its leading, for several substances, pretty accurately to the specific volumes, obtained by observation. It may be observed here, that they frequently consider as a series of confirmations, what is actually one confirmation only. A series of several bodies of analogous formulæ, possessing the same, or nearly the same specific volume, and to whose corresponding constituent a uniform specific volume is attributed, affords by no means a similar series of arguments for the correctness of an assumption; taken together, they constitute only *one*, (for, if the assumption agrees with one of these bodies, it *must*, whether right or wrong, agree with all the others), or no argument whatever, if the assumption has been made for such a body only, and not also for one of a different formula and different specific volume. The authors point out some additional coincidences; as above mentioned, 1·225 is considered by them as the number, the multiples of which are the specific volumes of the bodies; the number of units of volume ascribed to a body is obtained by dividing its specific volume by 1·225. Now they find, that the sulphates of the magnesia-series contain as many atoms of water of crystallization (in opposition to water of constitution; the authors represent, however, the former by the latter), as there are units of volume in the base; the phosphates and arseniates, on the other hand, as many as there are units of volume contained in the acid. This, however, they state, to have been most likely only accidental.

Specific Volume of similarly shaped Bodies.—Gerhardt(1) has given a synopsis of minerals, crystallising, in his opinion, in regular octohedrons, and represented, according to ordinary views, by a great variety of formulæ, (minerals of the group of spinell, martite, titanoferrite, periklase, perowskite, braunite). He states, that very nearly the same specific volume is found for all these minerals, if their formulæ be written in such a manner as to combine with every equivalent of oxygen one equivalent of metal of any kind, (for this, some of the usually adopted equivalents have, of course, to be altered). The result is rather startling, especially when we find in this synopsis, along with substances crystallizing in the regular system, compounds belonging to the square-prismatic system, (braunite, because its form differs but little from a regular octohedron,) and rhombohedral forms, (titanoferrite partly,) while the compositions adopted in many cases (as for chromo-ferrite of St. Domingo and periklase) are perfectly erroneous. Specific volume of similarly shaped bodies.

On the Condensation of Water when mixed with Acids.—Naumann(2) has published a paper on the condensation of the water-atoms in hydrated acids. He considers the following results as probable: If an acid, (hypothetically anhydrous,) containing *n* equivalents of oxygen, combines with water, the value of condensation *c*, (*i. e.* the difference of the specific volumes of water, in the mixture, and isolated,) of every newly added equivalent of water, (with the exception of the *n*th,) is given by the proportion $v : \phi = \phi : x$, v representing the specific volume of the acid previously to its receiving the new equivalent, ϕ the original specific volume of the water; for the *n*th equivalent of water itself Naumann gives the proportion $v : \psi = \psi : c$, in which v and c denote the same values, as before, ψ being the specific volume belonging, according to the preceding development, to the $(n - 1)$th equivalent in the mixture.—The author endeavours to trace this law by an examination of the statements made respecting the specific gravities of aqueous mixtures of nitric, acetic, and sulphuric acids; as to the two former acids, the indications agree with it; as to sulphuric acid, the older experiments of Dalton were found concordant; not those of Ure, but more so, the most recent ones by Bineau. Naumann's law is, that "within certain limits, the condensation of water, when mixed with an (aqueous) acid, diminishes, while the specific volume of the acid increases." His distinction of the first series of equivalents and the *n*th equivalent of water is artificial; and improbable, at least, is his expression of

(1) J. Pharm. [3] 381; Sill. Am. J. [2] IV, 405.
(2) J. Pr. Chem. XLIII, 1; Ann. Ch. Pharm. LXVIII, 218.

On the condensation of water when mixed with acids.

the regularity, if actually existing; for it would be necessary to assume that, in aqueous nitric acid (NO_5, + 4 HO,) the water was in, at least, 4 different states, (namely, each of the equivalents added to NO_5, HO with a peculiar specific volume).

THERMOLOGY.

Sources of Heat. Disengagement of Heat during Chemical Combination.—Andrews(1) states as the result of his researches on the heat evolved during metallic substitution, that when an equivalent of a metal replaces another in a solution of any of its salts of the same order, the heat developed is, with the same metals, constantly the same, the expression of a solution of the same order being understood to mean a solution in which the same kind of precipitate is produced by the addition of an alkali, or in which the metal exists in the same state of oxidation. The metallic salts, in the precipitation of which by other metals, the evolved heat was ascertained, were those of copper, precipitated by zinc, iron, or lead; of silver, precipitated by zinc or copper; and of lead, mercury, and platinum, precipitated by zinc; the acids were sulphuric, hydrochloric, acetic, and formic acids. A further deduction is this: that, if three metals, A, B and C be so related, that A is capable of displacing B and C from their combinations, and also B capable of displacing C, then the heat developed in the substitution of A for C, will be equal to that developed in the substitution of A for B, added to that developed in the substitution of B for C.

Andrews(2) has also again determined the quantity of heat which is disengaged in the combination of bodies with oxygen and chlorine. The combination of the gases with oxygen took place in a copper vessel of about 380 cub. cent. capacity, and was induced by the electric ignition of a fine platinum wire. The copper vessel was immersed into a water-calorimeter, which, after having been perfectly closed, was suspended in a wide cylinder, capable of being rapidly rotated round its horizontal axis. By this rotation, which was performed both before and after the combination of the gases, it was intended to establish a complete uniformity of temperature in the water of the calorimeter. If, in the combination of two gases, water was generated, the heat evolved in the condensation of the vapour had to be subtracted. The results are contained in the following table, in

(1) Phil. Mag. [3] XXXII, 392. (2) Phil. Mag. [3] XXXII, 321, 426.

which the quantity of heat necessary to raise the temperature of 1 grm. of water through 1^0, is taken as unit:

Sources of heat. Disengagement of heat during chemical combination.

Name of the gas.	Heat of combustion.					
	Of 1 litre of the gas with oxygen.	Deviation from the mean.	Of 1 litre of oxygen with the gas.	Of 1 grm. of oxygen with the gas.	Corrected for aqueous vapour.	Of 1 grm. of the gas with oxygen.
Hydrogen . . .	3036	16	6072	4226	3539	33808
Carbonic oxide .	3057	6	6114	4255	—	2431
Marsh gas . . .	9421	10	4716	3277	2931	13108
Olefiant gas . .	15016	40	5005	3483	3252	11942

The combination of solid and liquid bodies with oxygen was conducted in a cup of platinum or porcelain, suspended by means of platinum wires in a copper vessel of about 4 litres capacity, which was filled with oxygen. The whole was introduced into a water-calorimeter, in the cooling-water of which it was gently moved up and down, in order to produce an uniform distribution of heat through the apparatus. In these experiments, the inflammation was also effected by a platinum wire, ignited by means of the electric current. The corrections necessary on account of the cooling or heating influence of the surrounding air, were so small in each case, that they could be made on some simple assumptions. The results are as follows:

Substance.	Number of experiments.	Heat of combustion.			
		1 grm. of the substance with oxygen.	Deviation from the mean.	1 grm. of oxygen with the substance.	1 litre of oxygen with the substance.
Wood-charcoal	8	7678	121	2879	4137
Sulphur	4	2307	31	2307	3315
Alcohol	4	6850	98	3282	4716
Phosphorus	3	5747	59	4509	6479
Zinc	3	1301	4	5366	7710
Iron	3	—	—	4134	5940
Tin	3	—	—	4230	6078
Protoxide of tin	3	521	3	4349	6249
Copper	3	—	—	2394	3440
Suboxide of copper . . .	3	256	6	2288	3288

To effect the combustion of the metals, a small quantity of phosphorus (about 8 milligrm.) was added, whose heat of combustion

Sources of heat. Disengagement of heat during chemical combination.

had to be deducted.—The most important determination, is that of the heat disengaged in the combustion of carbon. Andrews prepared this by boiling wood-charcoal in nitro-hydrochloric acid, and then exposing it for several hours at a slow red heat to the action of dry chlorine, and ultimately to a white heat under a layer of charcoal; the platinum capsule was weighed again after the experiment; a certain amount of unburned carbon remaining behind along with the earthy impurities, notwithstanding the great excess of oxygen. Dulong had found (as a mean) 7288 units, Despretz 7912, Lavoisier 7624, Favre and Silbermann:

	Spec. heat according to Regnault.	Heat of combination.
For Diamond	0·147	7824
„ Graphite	0·201	7778
„ Wood-charcoal	0·242	8080

Some later experiments of Andrews, in which the carbon was burned in a platinum cage, only $\frac{1}{100}$th being converted into carbonic oxide, gave 7860 units, or, corrected for the carbonic oxide formed, 7881 units.

The conclusion to which some physicists had been led by Dulong's results, namely, that the heat disengaged in the combustion of a compound gas was equal to that evolved in the combustion of its constituents, must be considered as refuted by the numbers above communicated. By calculating on this hypothesis, the heat of combustion of 1 litre of vapour of carbon, from the results obtained with marsh-gas and olefiant gas, we arrive at two very different numbers:

	Dulong.	Andrews.		Dulong.	Andrews.
1 litre of marsh gas . .	9588	9420	1 litre of olefiant gas. .	15338	15014
2 litres of hydrogen . .	6212	6072	2 litres of hydrogen . .	6212	6072
1 litre of vapour of carbon	3376	3348	1 litre of vapour of carbon	4563	4471

To induce the combination with chlorine, the substances, enclosed in hermetically sealed and very fragile little glass balls, were introduced into a glass vessel, the air of which was afterwards expelled by dry chlorine. After immersion of the glass vessel in the copper calorimeter the glass balls were broken by a sudden concussion. Both the apparatus and method of experiment resembled those used in the case of oxygen. The combination of potassium and chlorine took place in a brass vessel, which was not sensibly attacked by dry chlorine.—Zinc combined with chlorine only in the presence of water, and it was necessary to deduct, from the result of obser-

Sources of heat. Disengagement of heat during chemical combination.

vation, the heat disengaged by the chloride of zinc, when dissolving in the water. The following are the results:

	Chlorine.			Substance.
	1 litre.	1 grm.	1 equiv.	1 grm.
Potassium . .	9329	2943	13008	2655
Tin	2844	897	3966	1079
Antimony . .	2726	860	3804	707
Arsenic . . .	2232	704	3114	994
Mercury . . .	2605	822	3633	—
Phosphorus . .	1925	607	2683	3422 ?
Zinc	4524	1427	6309	1529
Copper . . .	2734	859	3805	961
Iron	2920	921	4072	1745

Many of these bodies, as iron, antimony, tin, and zinc, (the latter in a less striking manner), appear to evolve equal quantities of heat when combining with either oxygen or chlorine.—The opinion that the above thermal effects are equal to those which are produced in the reaction of these bodies upon each other in the moist way, is supported as yet by one instance only. The heat disengaged in precipitating metallic copper from a solution by means of zinc, should be equal to the difference of the quantities of heat evolved in the combinations of zinc and of copper, respectively, with oxygen, added to that, which is developed by the substitution of protoxide of zinc for protoxide of copper. We have (Zn with O) — (Cu with O) = 5366 — 2394 = 2972, and by adding 353, arising from substitution of one oxide for the other, we obtain 3325 units of heat, a number sufficiently agreeing with the result of observation 3435. On the other hand we have:

	Compound dry.	Compound in solution.
Zn with Cl . . .	6309	7025
Cu with Cl . . .	3805	4167
	2504	2858

Neither of these numbers agrees with 3325, the amount disengaged in the substitution of zinc for copper. The thermal effects are, therefore, not favourable to the hypothesis, that the metallic chlorides exist, as such, in solution.

Favre and Silbermann(1) in continuing their researches on the heat evolved in chemical combinations, have arrived at the following results:

1. In the decomposition of calcareous spar by heat 308·1 units of

(1) Compt. Rend. XXIV, 1081.

Sources of heat. Disengagement of heat during chemical combination.

heat were absorbed; the conversion of arragonite into calcareous spar gave rise to a disengagement of 38·3 units; in the decomposition of arragonite 299·2 units were absorbed.

2. In the decomposition of protoxide of nitrogen into its constituents, the evolution of 1 grm. of oxygen was attended with a disengagement of 1090·5 units.

3. In the decomposition of binoxide of hydrogen, a disengagement of 1303 units took place, to which have to be added somewhat more than 600 units consumed in the gasification of the oxygen: together about 1950 units..

4. Evolution of heat in mixing 1 grm. of SO_4 H (hydrated sulphuric acid) with water:

With the first . $\frac{1}{8}$ eq. of w.	9·4	With 1 eq. of w.	61·7	With 7 eq. of w.	141·8
„ „ second $\frac{1}{8}$ „ „	8·8	„ 2 „ „	94·6	„ 8 „ „	145·1
„ „ first . $\frac{1}{4}$ „ „	18·8	„ 3 „ „	111·9	„ 9 „ „	148·5
„ „ second $\frac{1}{4}$ „ „	17·2	„ 4 „ „	122·2	„ 10 „ „	148·4
„ „ first . $\frac{1}{2}$ „ „	36·7	„ 5 „ „	130·7	„ 20 „ „	148·7
„ „ second $\frac{1}{2}$ „ „	28·3	„ 6 „ „	136·2		

Evolution of heat, in mixing 1 grm. of SO_4 H + HO with the first $\frac{1}{4}$ eq. 9·2, with the second $\frac{1}{4}$ eq. 7·8; with the first $\frac{1}{2}$ eq. 17·3, with the second $\frac{1}{2}$ eq. 12·3. Evolution of heat, in mixing 1 grm. of SO_4 H + 2HO with the first $\frac{1}{2}$ eq. of water 9·5, with the second $\frac{1}{2}$ eq. 7·6.

5. Evolution of heat in the combinations of bases with acids in equivalent proportions, the acids highly diluted and in great excess.

1 grm. of hydrate of lime saturated with		1 grm. of potassa, diluted with water, saturated with			
Sulphuric acid . . .	669·2	Sulphuric acid . .	311·8	Phosphoric acid	323·9
Hydrochloric acid . .	603·2	Nitric acid . . .	312·5	Acetic acid . .	283·5
Nitric acid	607·0	Hydrochloric acid .	314·4	Citric acid . .	268·3
Acetic acid	518·2	Metaphosphoric .	325·4		

1 grm. of soda, dilute, saturated with		1 grm. of ammonia, dilute, saturated with		1 grm. of strontia, dissolved, saturated with	
Sulphuric acid . .	464·3	Sulphuric acid . .	529·7	Hydrochloric acid .	184·7
Nitric acid . . .	470·8	**1 grm. of baryta, dissolved, saturated with:**		**Protoxide of iron precipitated with 1 grm. of ammonia** . . .	71·7
Hydrochloric acid .	465·3	Hydrochloric acid .	181·7	**1 grm. of protoxide of iron ditto** . . .	323·4
Metaphosphoric acid	474·4	Acetic acid . . .	158·5		
Phosphoric acid . .	480·1	**1 grm. of crystallized baryta in 4·460 grm. of water, saturated with acetic acid**	80·7		
Formic acid . . .	407·7				
Acetic acid . . .	418·0				
Valerianic acid . .	414·1				
Citric acid . . .	103·7				

In forming acid salts, Favre and Silbermann worked with

Sources of heat.

Disengagement of heat during chemical combination.

2 decigrm. of potassa and soda; the flask contained 12cc. of water. The following numbers refer to 1 grm. of base:

1. Potassa with oxalic acid.		2. Soda with oxalic acid.		3. Potassa with tartaric acid.	
1 eq. of acid 287·5		1 eq. 428·2		1 eq. 264	
2 „ „ „ 285·1	much w.	2 „ 619·4	much water.	2 „ 455·2	much water.
345·6	little water.	4 „ 688·0	much water.	480.6	little water.
354·6		650·1	saturated with water.	8 „ 482·0	
4 „ „ „ 579·8	the flask filled with w.	707·4			
617·0					
610·0					

4. Soda with tartaric acid.

1 eq. of acid 392·4		4 eq. 392·1	much water.
2 „ „ „ 387·1	much water.	596·1	little water.
586·9	little water.	1 „ 413·7	much water.
		590·0	little water.

6. Alumina, sesquioxide of iron, and sesquioxide of uranium, when precipitated by 1 grm. of ammonia disengaged 134·2, 295·8, 518·5 units, or, reduced to 1 grm. of the oxides, 605·2, 234·3, 2·1.

7. Hence the equivalents of bases evolve the following quantities of heat:

Lime	607	Potassa	539	Baryta	492	Protoxide of iron	404	Alumina	1113
Soda	520	Ammonia	492	Strontia	343	Sesquioxide of iron	661	Sesquioxide of uranium	11

8. The following table contains the quantities of heat absorbed in dissolving 1 grm. of the following crystals:

Nitrate of ammonia	63·3	Sulphate of lime	23·1
„ „ soda	43·6	„ „ lime dissolved in sulphate of ammonia	0·0
„ „ potassa	66·9	Potassa-alum	22.4
„ „ strontia	39·3	Ammonia-alum	18·2
„ „ lime	25·7	Acetate of soda	26·9
Chloride of sodium	8·5	„ „ potassa	+ 11·6
„ „ potassium	47·6	„ „ „ acid	18·5
„ „ barium	16·1	„ „ lime	+ 21·9
„ „ strontium	23·8	„ „ baryta	3·3
„ „ ammonium	66·2	Oxalic acid (cryst.)	58·7
„ „ calcium	14·6	Oxalate of potassa	36·9
Sulphate of potassa	33·3	„ „ „ (acid)	59·5
„ „ soda	47·1	Carbonate of potassa	+ 2·5
„ „ alumina	+ 12·7	„ „ „ (acid)	49·1
„ „ ammonia	10·4	„ „ soda	49·8
„ „ sesquioxide of uranium	+ 10·2	Tartaric acid (cryst.)	18·8
„ „ potassa (acid)	24·3	Tartrate of potassa	16·5
„ „ protoxide of iron	11·6	„ „ soda	24.2
„ „ protoxide of iron and potassa	20·6	„ „ potassa and soda	39·3
„ „ baryta	52·2	Phosphate of soda	49·4
„ „ strontia	58·4	Pyrophosphate of soda	21·1

The sign + indicates an evolution of heat. In mixing sulphate of iron with sulphate of potassa, sulphate of iron with sulphate of

Sources of heat. Disen- t du- ing c cal cor. nath.

ammonia, sulphate of alumina with sulphate of soda, sulphate of alumina with sulphate of potassa, sulphate of alumina with sulphate of ammonia, tartrate of soda with tartrate of potassa, no calorific effect became perceptible.

Among the conclusions to which the authors of this investigation have been led by their results, we point out the following as characteristic,—1. That a neutral salt T, in solution, and in the crystalline state, constitutes two isomeric bodies, *e. g.* SO_4 K and S_2 O_8 K_2; 2. That the acid salts and double salts are formed only during crystallization; they were the crystallized neutral salts "*M^2 du type remplacé par des M quelconques;*" 3. That a new support has been given to the opinion, which considers the latent fusion-heat in water as the result of a chemical process, HO in ice passing into n (HO), where n represents any simple number. It is not the first time that the valuable observations(1) of MM. Favre and Silbermann are associated with conclusions, the necessary connection of which, with the former, is not evident. The heat disengaged during the combustion of bisulphide of carbon, and of carbon in protoxide of nitrogen, has led them to the theory of the splitting (*dédoublement*) of the elements, a doctrine which they appear to develope with daily increasing vigour.

Another paper(2) is devoted to the investigation of the heat evolved during the substitution, in solutions, of one metal for another, or of oxides for each other. The chemical reaction was conducted in a flask provided with a serpentine (to cool the hydrogen evolved in several cases) and a safety-tube (for pouring in the acid).

grm. of	when acted on by	gives	evolving units of heat
Zinc	SO_4 H	SO_4 Zn + H	520
Zinc	NO_6 Ag	NO_6 Zn + Ag	1187
Zinc	SO_4 Cu	SO_4 Zn + Cu	693
Zinc	$C_4 H_3 O_4$ Pb	$C_4 H_3 O_4$ Zn + Pb	466
Copper	NO_6 Ag	NO_6 Cu + Ag	501
Iron	SO_4 Cu	SO_4 Fe + Cu	647

The heat evolved in the substitution of zinc for silver was indirectly ascertained, the latter being first replaced by copper, and then again by zinc, 501 + 693 amounts nearly to 1187.—To deduce from the above result the heat of combustion of the metals, it is necessary to add the heat developed in the conversion of the replaced metal into oxide, and of the oxide into hydrate, and in the combinations of the latter with the anhydrous acid; whilst the heat disengaged, by the replacing

(1) Compt. Rend. XXII, 823, 1140; XXIII, 199, 411. (2) Ibid. XXVI. 595.

Sources of heat
Disengagement of heat during chemical combination.

metal, in the conversion of its oxide into hydrate, and in the combination of the hydrate with the anhydrous acid, has to be deducted. Favre and Silbermann ascertained, that, when combining with dilute acids, 1 grm. of precipitated oxide, (anhydrous, or in the state of hydrate,) disengages the following number of heat-units,

HO with any acid	0	CuO with Sulphuric acid	185
ZnO with Sulphuric acid	241	CuO with Nitric acid	148
ZnO with Nitric acid	206	PbO with Acetic acid	61
ZnO with Hydrochloric acid	204	AgO with Nitric acid	51
ZnO with Acetic acid	179	ZnO with concen. hydrochloric acid (anhydrous)	245
FeO with Sulphuric acid	291		

Hence the heat of combustion of the metals is found to be

	1 grm.	1 eq.		1 grm.	1 eq.
Hydrogen	34462	34462	Copper	655	21280
Iron	1332	35964	Lead	255	26520
Zinc	1277	41503	Silver	49	5292

Mechanical Equivalent of Heat.—Joule(1) has determined the mechanical equivalent of heat by comparing the heat evolved by the friction of a horizontal paddle-wheel, with the force necessary to effect the rotation of the wheel. A brass wheel was moved by means of a descending weight, in one series of experiments in water, in another series in sperm oil; as a mean of nine experiments in each series, the mechanical equivalent of the heat-unit was found to be 428 and 429 metregrammes(2). A third series of experiments(3), in which an iron wheel was moved in mercury, gave, as average of six experiments, 432·1. A claim to priority on the part of Mayer(4) induced Joule(5) to publish a synopsis of his researches upon this subject, in which he insists upon the priority of his inquiry. In attributing the mechanical effect of the expansion of gases entirely to the heat of expansion as determined by Dulong ($0^0 \cdot 421$ for a compression of $\frac{1}{273}$), the mechanical equivalent is found to be only 368·5 metregrammes, and we are the more inclined to believe that a loss of heat in Joule's experiments has given too high a number for the mechanical equivalent, since a test, which appeared to Joule(6) a corroboration of his determinations, when more minutely investigated, leads to an opposite result. If we assume, with Joule, the mechanical equivalent of heat to be 430 metregrammes, the ratio of the specific heat of air at constant volume to that at constant pressure is found equal to 1·077; and the square root of this number, when multiplied by Newton's velocity of sound 280^m gives $290^m \cdot 4$, a result considerably below truth.

(1) Phil. Mag. [3] XXXI, 173.
(2) 1 grm. raised 1 metre, or 0·0072348 lbs. raised 1 foot.
(3) Compt. Rend. XXV, 309.
(4) Compt. Rend. XXVI, 385.
(5) Compt. Rend. XXVIII, 132.
(6) Phil. Mag. XXXI, 114.

Mechanical equivalent of heat. Seguin(1) communicates a contribution to the determination of the mechanical equivalent of heat. He calculates the mechanical effect, exerted by steam of 180°, while it expands and cools to 80°, part of its free heat becoming latent as heat of expansion. The unit of heat exerts

between	180°	and	160°	an effect of	395	metregrammes.
„	160	„	140	„	412	„
„	140	„	120	„	440	„
„	120	„	100	„	472	„
„	100	„	80	„	529	„

or, as a mean, a mechanical effect of 449 grm., which are raised to the height of 1 metre. Seguin announces, that he is engaged in an extensive series of investigations, in order to demonstrate that the phenomena of heat are only phenomena of motion, and consequently subject to the law of general gravitation.

Expansion of solid Bodies by Heat.—Joule and Playfair(2) have endeavoured to determine the expansion of several solid bodies. For this purpose little glass bottles were used, as employed in the determination of specific gravities. The expansion of the glass was found, by filling a bottle of this kind with water, and inserting a graduated thermometer tube as stopper; the water in the tube stood at the same point at 3°·84 and 7°·67; hence, the expansion of the glass within this interval of temperature is equal to that of the water between the same limits; the result of Despretz being adopted for the latter, the cubic expansion of glass between 0° and 100° was found to be equal to 0·002788. Another experiment, made in the same manner, gave 0·002798.

It was then ascertained how much oil of turpentine a bottle was capable of holding at different temperatures. The expansion of solid bodies was determined in the following manner: the bottle, partially filled with oil of turpentine, was weighed, and a quantity of the substance under examination having been introduced, its weight was again determined. After having removed, by means of an air-pump, the air adhering to the substance, the vacant space in the bottle was filled up with oil of turpentine, and the thermometer-tube inserted as a stopper. Ultimately, the weight of the bottles filled at different temperatures (between 3°5 and 31°5) was ascertained. From these observations it was possible to calculate how much space the substance, under examination, occupied at different temperatures, and consequently its expansion between 0° and 100°. The authors state, as the result of many experiments, that the expansion of salts was found to be uniform. The specific gravity of the oil of

(1) Compt. Rend. XXV, 420. (2) Chem. Soc. Mem. I. 121.

turpentine having been ascertained, these experiments also gave the specific gravities of the substances investigated. The following are the results of their observations :

Expansion of solid bodies by heat.

Substance.	Formula.	Cubic expansion 0 — 100°.	Spec. grav. at 3°·9.
Copper	Cu	0·0055	8·367
Ditto	„	0·00767	8·416
Protoxide of mercury . .	$Hg\,O$	0·00580	11·136
„ „ lead . . .	$Pb\,O$	0·00795	9·363
Protosesquiox. of manganese .	$Mn_3\,O_4$	0·00522	4·325
Binoxide of tin . . .	$Sn\,O_2$	0·00172	6·712
Protosulphide of lead . .	$Pb\,S$	0·01045	6·924
Chloride of potassium . .	$K\,Cl$	0·01094	1·978
„ „ barium . .	$Ba\,Cl + 2\,HO$	0·00987	3·054
„ „ ammonium . .	$NH_4\,Cl$	0·0191	1·533
Nitrate of soda . . .	NaO, NO_5	0·0128	2·261
„ „ potassa . . .	KO, NO_5	0·01967	2·108
„ „ ditto . . .	„	0·01724	2·096
„ „ ditto . . .	„	0·01949	2·107
„ „ protoxide of lead .	PbO, NO_5	0·00839	4·472
„ „ baryta . . .	BaO, NO_5	0·00452	3·161
Chlorate of potassa . .	KO, ClO_5	0·01711	2·326
Chromate of potassa . .	KO, CrO_3	0·01134	2·711
Ditto	„	0·01101	2·723
Bichromate of potassa . .	$KO, 2\,CrO_3$	0·0122	2·692
Bichromate of chl. of potassium	$KCl + 2\,CrO_3$	0·01590	2·497
Oxalic acid	$HO, C_2\,O_3 + 2\,HO$	0·02748	1·641
Oxalate of potassa . . .	$KO, C_2\,O_3 + HO$	0·01162	2·127
Binoxalate of potassa . .	$KO, 2\,C_2\,O_3 + 3\,HO$	0·01134	2·044
Quadroxalate of potassa . .	$KO, 4\,C_2\,O_3 + 7\,HO$	0·01592	1·849
Oxalate of ammonia . .	$NH_4\,O, C_2\,O_3 + HO$	0·00876	1·500
Binoxalate of ammonia . .	$NH_4\,O, 2\,C_2\,O_3 + 3\,HO$	0·01372	1·613
Quadroxalate of ammonia .	$NH_4\,O, 4\,C_2\,O_3 + 7\,HO$	0·01435	1·652
Sulphate of potassa . .	KO, SO_3	0·01070	2·656
Bisulphate of potassa . .	$KO, SO_3 + HO, SO_3$	0·01229	2·478
Sulphate of ammonia . .	$NH_4\,O, SO_3$	0·01093	1·761
Sulphate of protoxide of cop. .	$CuO, SO_3 + 5\,HO$	0·00953	2·290
Ditto	„	0·00532	2·242
Ditto	„	0·00812	2·278
Sulphate of protoxide of iron .	$FeO, SO_3 + 7\,HO$	0·01153	1·883
„ of magnesia . . .	$MgO, SO_3 + 7\,HO$	0·01019	1·689
„ of protox. of cop. & ammo.	$CuO, SO_3 + NH_4\,O, SO_3 + 6\,HO$	0·00661	1·894
„ „ „ „ „ potassa	$CuO, SO_3 + KO, SO_3 + 6\,HO$	0·00904	2·164
„ of magnesia and potassa .	$MgO, SO_3 + KO, SO_3 + 6\,HO$	0·00937	2·053
„ of sesquiox. of chromium and potassa	$Cr_2\,O_3, 3\,SO_3 + KO, SO_3 + 24\,HO$	0·00524	1·856
„ of alumina and potassa .	$Al_2\,O_3, 3\,SO_3 + KO, SO_3 + 24\,HO$	0·00368	1·751
„ of protoxide of zinc and potassa	$ZnO, SO_3 + KO, SO_3 + 6\,HO$	0·00824	2·240
„ of magnesia and ammonia	$MgO, SO_3 + NH_4\,O, SO_3 + 6\,HO$	0·00716	1·717
Cane sugar	$C_{12}\,H_{11}\,O_{11}$	0·01116	1·593
Sugar of milk . . .	$C_{12}\,H_{12}\,O_{12}$	0·00911	1·534

If several experiments were made with the same substance, the expansions observed exhibited rather considerable discrepancies.

Expansion of solid bodies by heat.

Joule and Playfair believe that these discrepancies arise from an actual difference in the physical properties of the substances examined; the copper, (reduced from the oxide by means of hydrogen) in one experiment, had been exposed to a higher temperature than in the other; the nitrate of potassa had been partly employed in large crystals enclosing a certain quantity of water, partly in small ones, &c. However, the expansion of the nitre containing water was found inferior to that of the anhydrous crystals, a fact which could have scarcely been expected; it is very probable that the discrepancies in the results, obtained with the same substance, have to be attributed to the method; and that these results, as far as the expansion is concerned, require confirmation or correction.

In three series of experiments, independent of each other, Schumacher, Pohrt, and Moritz(1) have found the linear expansion of ice for an interval of 100° to be 0·00524, 0·00513, and 0·00518. (Brunner's experiments had given the number 0·00375, those of Marchand the number 0·0035.)

Expansion of liquid Bodies by Heat.—Pierre has published several papers upon the expansion of liquids: a subject more extensively investigated by him than by any other inquirer. The first of these papers has appeared previously to the time when this report commences; we will, nevertheless, give the results contained therein, in order to form a complete synopsis of Pierre's experiments upon expansion.

It may be stated at once, that the method of preparing, and, in most cases, the analysis of the substances investigated has been given, that the specific gravity was taken for 0°, and that the atmospheric pressure was ascertained at the time of determining the boiling point. The investigation of the expansion was made according to the thermometrical method; the details of the manner of experimenting and calculating are accurately described by Pierre, in the introduction to his first paper(2). We report the result obtained with each body, the formula, which gives the true volume V for a temperature t°, the volume at 0° = 1, and add in brackets the limits of temperature, within which the experiments were instituted.

In the first memoir, Pierre communicates the expansion of the following liquids:

Water. (HO). The memoir gives only the numerous individual experiments made with this substance, the communication of which would exceed the limits of this report. Pierre found no formula ac-

(1) From: Arch. f. wissenschaftl. Kunde v. Russland, VII. 333, in Arch. Ph. Nat. X, 47.

(2) Ann. Ch. Phys. [3] XV, 325.

curately representing the expansion of water from — 13^0 to 100^0, nor has he deduced from his experiments a table in which the expansions for uniformly increasing temperatures could be seen. Expansion of liquid bodies by heat.

Alcohol (spirits of wine, hydrated oxide of ethyl; $C_4\ H_6\ O_2$). Spec. grav. 0·8151. Boiling point $78^0{\cdot}3$ at 758^{mm}.

$$V = 1 + 0{\cdot}0010186\,t + 0{\cdot}00000171510\,t^2 + 0{\cdot}000000001345\,t^3\ (-32^0{\cdot}2 \text{ to } +76^0{\cdot}6)$$

Pyroxylic spirit (hydrated oxide of methyl; $C_2\ H_4\ O_2$). Spec. grav. 0·8207. Boiling point $66^0{\cdot}3$ at 759^{mm}.

$$V = 1 + 0{\cdot}0011856\,t + 0{\cdot}0000015649\,t^2 + 0{\cdot}000000009111\,t^3\ (-38^0{\cdot}0 \text{ to } +69^0{\cdot}4)$$

Bisulphide of carbon ($C\ S_2$). Spec. grav. 1·2931. Boiling point $17^0.9$ at $755^{mm}{\cdot}8$.

$$V = 1 + 0{\cdot}0011398\,t + 0{\cdot}0000013707\,t^2 + 0{\cdot}000000019123\,t^3\ (-34^0{\cdot}9 \text{ to } 59^0{\cdot}6)$$

Ether (oxide of ethyl; $C_4\ H_5\ O$). Spec. grav. 0·7358. Boiling point $35^0{\cdot}5$ at $755^{mm}{\cdot}8$.

$$V = 1 + 0{\cdot}0015132\,t + 0{\cdot}0000023592\,t^2 + 0{\cdot}000000040051\,t^3\ (-15^0{\cdot}4 \text{ to } +38^0{\cdot}1)$$

Hydrochloric ether (chloride of ethyl; $C_4\ H_5\ Cl$). Spec. grav. 0·9214. Boiling point 11^0 at 758^{mm}.

$$V = 1 + 0{\cdot}0015746\,t + 0{\cdot}0000028137\,t^2 + 0{\cdot}000000015698\,t^3\ (-31^0{\cdot}6 \text{ to } +26^0.4)$$

Hydrobromic ether (bromide of ethyl; $C_4\ H_5\ Br$). Spec. grav. 1·4733. Boiling point $40^{\cdot 0}7$ at 757^{mm}.

$$V = 1 + 0{\cdot}0013376\,t + 0{\cdot}0000015013\,t^2 + 0{\cdot}000000016900\,t^3\ (-31^0{\cdot}9 \text{ to } +53^0{\cdot}7)$$

Hydriodic ether (iodide of ethyl; $C_4\ H_5\ I$). Spec. grav. 1·9755. Boiling point 70^0 at $751^{mm}{\cdot}7$.

$$V = 1 + 0{\cdot}0011423\,t + 0{\cdot}0000019638\,t^2 + 0{\cdot}000000006206\,t^3\ (-34^0{\cdot}8 \text{ to } 71^0{\cdot}9)$$

Bromide of methyl ($C_2\ H_3\ Br$). Spec. grav. 1·6644. Boiling point about 13^0 at 759^{mm}.

$$V = 1 + 0{\cdot}0014152\,t + 0{\cdot}0000033153\,t^2 + 0{\cdot}00000011381\,t^3\ (-34^0{\cdot}6 \text{ to } 27^0{\cdot}8)$$

Iodide of methyl ($C_2\ H_3\ I$). Spec. grav. 2·1992. Boiling point $43^0{\cdot}8$ at $750^{mm}{\cdot}2$.

$$V = 1 + 0{\cdot}0011996\,t + 0{\cdot}0000021633\,t^2 + 0{\cdot}000000010051\,t^3\ (-35^0{\cdot}4 \text{ to } 61^0{\cdot}5)$$

Formic ether (formiate of oxide of ethyl; $C_6\ H_6\ O_4$). Spec. grav. 0·9357. Boiling point $52^0{\cdot}9$ at 752^{mm}.

$$V = 1 + 0{\cdot}0013252\,t + 0{\cdot}0000028625\,t^2 + 0{\cdot}0000000066180\,t^3\ (-32^0{\cdot}4 \text{ to } 61^0{\cdot}6)$$

Acetate of oxide of methyl ($C_6\ H_6\ O_4$). Spec. grav. 0·8668 (?). Boiling point $59^0{\cdot}5$ at $761^{mm}{\cdot}2$.

$$V = 1 + 0{\cdot}0012960\,t + 0{\cdot}0000029098\,t^2 + 0{\cdot}000000004257\,t^3\ (-34^0{\cdot}3 \text{ to } 66^0{\cdot}3.)$$

In a second paper(1) the author has communicated the investigation of the following liquids:

(1) Ann. Ch. Phys. [3] XIX, 193; abstracted Ann. Ch. Pharm. LXIV. 160.

Expansion of liquid bodies by heat.

Fusel oil (potato-oil, hydrated oxide of amyl; $C_{10}\ H_{12}\ O_2$). Spec. grav. 0·8271. Boiling point 131°·8 at 751mm·3.

$$V = 1 + 0{\cdot}00089001\,t + 0{\cdot}00000065729\,t^2 + 0{\cdot}000000011846\,t^3\ (0^0 \text{ to } 80^0)$$
$$V = 1 + 0{\cdot}00089885\,t + 0{\cdot}00000068745\,t^2 + 0{\cdot}000000010096\,t^3\ (80^0 \text{ to } 130^0)$$

Pierre calculates the expansion up to 80° by means of the first, that beyond 80° by means of the second formula; *one* formula failing to express his observations accurately enough for the whole interval between 0 and 130°.

Acetic ether (acetate of oxide of ethyl; $C_8\ H_8\ O_4$). Spec. grav. 0·9069. Boiling point 74°·1 at 766mm·5.

$$V = 1 + 0{\cdot}0012585\,t + 0{\cdot}0000029569\,t^2 + 0{\cdot}000000001492\,t^3\ (-36^0{\cdot}2 \text{ to } 72^0{\cdot}4)$$

Butyrate of oxide of methyl ($C_{10}\ H_{10}\ O_4$). Spec. grav. 1·0293. Boiling point 102°·1 at 743mm. (Both properties differ considerably from those observed by H. Kopp, Comp. p. 50).

$$V = 1 + 0{\cdot}0012399\,t + 0{\cdot}000000626025\,t^2 + 0{\cdot}000000013066\,t^3\ (0^0 \text{ to } 99^0{\cdot}8)$$

Butyric ether (butyrate of oxide of ethyl; $C_{12}\ H_{12}\ O_4$). Spec. grav. 0·9019. Boiling point 119° at 746mm·5.

$$V = 1 + 0{\cdot}0012028\,t + 0{\cdot}00000007223\,t^2 + 0{\cdot}00000002263\,t^3\ (0^0 \text{ to } 100^0)$$
$$V = 1 + 0.0006327\,t + 0{\cdot}000012763\,t^2 + 0{\cdot}00000005028\,t^3\ (100^0 \text{ to } 118^0)$$

A third paper(1) contains the investigation of the following liquids:

Terchloride of phosphorus ($P\ Cl_3$). Spec. grav. 1·6162. Boiling point 78°·3 at 751mm·5.

$$V = 1 + 0{\cdot}0011286\,t + 0.00000087288\,t^2 + 0.000017921\,t^3\ (-35^0{\cdot}7 \text{ to } + 74^0{\cdot}9)$$

Terbromide of phosphorus ($P\ Br_3$). Spec. grav. 2·9249. Boiling point 175°·3 at 760mm·2.

$$V = 1 + 0{\cdot}00084720\,t + 0{,}00000043672\,t^2 + 0{\cdot}000000002528\,t^3\ (0^0 \text{ to } 100^0)$$
$$V = 1 + 0{\cdot}00082127\,t + 0{\cdot}00000091431\,t^2 + 0{\cdot}000000000355\,t^3\ (100^0 \text{ to } 175^0)$$

Terchloride of arsenic ($As\ Cl_3$). Spec. grav. 2·2050. Boiling point 133°·8 at 756mm·9.

$$V = 1 + 0{\cdot}00097907\,t + 0{\cdot}00000096695\,t^2 + 0{\cdot}0000000017772\,t^3\ (-14^0{\cdot}9 \text{ to } 130^0{\cdot}2)$$

Bichloride of tin ($Sn\ Cl_2$). Spec. grav. 2·2671. Boiling point 115°·4 at 753mm·1.

$$V = 1 + 0{\cdot}0011328\,t + 0{\cdot}00000091171\,t^2 + 0{\cdot}0000000075798\,t^2\ (-19^0{\cdot}1 \text{ to } 112^0\,6)$$

Bichloride of titanium ($Ti\ Cl_2$). Spec. grav. 1·7609. Boiling point 136° at 762mm·3.

$$V = 1 + 0{\cdot}000942569\,t + 0{\cdot}0000013458\,t^2 + 0{\cdot}000000000888\,t^2\ (-22^0{\cdot}1 \text{ to } 134^0{\cdot}2)$$

Terchloride of silicium ($Si\ Cl_3$). Spec. grav. 1·5237. Boiling-point 59° at 760mm·1.

$$V = 1 + 0{\cdot}0012941\,t + 0{\cdot}0000021841\,t^2 + 0{\cdot}000000040864\,t^3\ (-32^0{\cdot}4 \text{ to } 58^0{\cdot}6)$$

(1) Ann. Ch. Phy. [3] XX, 5; abstracted Ann. Ch. Pharm. LXIV, 168,

Terbromide of silicium ($Si\ Br_3$). Spec. grav. 2·8128. Boiling point 153°·4 at 762^{mm}·5. Expansion of liquid bodies by heat.

$$V = 1 + 0{\cdot}00095257\,t + 0{\cdot}00000075674\,t^2 + 0{\cdot}0000000002921\,t^3\ (0^0 \text{ to } 149.^0 5).$$

Chloride of elayl (oil of olefiant gas, Dutch liquid; $C_4\ H_4\ Cl_2$). Spec. grav. 1·2803. Boiling point 84°·9 at 761^{mm}·9.

$$V = 1 + 0{\cdot}0011189\,t + 0{\cdot}0000010469\,t^2 + 0{\cdot}000000010341\,t^3\ (-22^0{\cdot}7 \text{ to } +83^0{\cdot}8)$$

Bromide of elayl ($C_4\ H_4\ Br_2$). Spec. grav. 2·1629 at 20°·8 (solidifies at 13°). Boiling point 132°·6 at 756^{mm}·9. The formulæ:

$$V = 1 + 0{\cdot}00095270\,d + 0{\cdot}0000013165\,d^2 + 0{\cdot}0000000010627\,d^3\ (20^0 \text{ to } 100^0)$$
$$V = 1 + 0{\cdot}0010168\,d + 0{\cdot}00000010223\,d^2 + 0{\cdot}000000008788\,d^3 +\ (100^0 \text{ to } 132^0{\cdot}6)$$

give the volume for a temperature (the former between 20° and 100°, the latter between 100° and 132°·6) which is d° higher than 20°·09, the volume at the latter temperature being = 1.

Bromine (Br). Spec. grav. 3·1872. Boiling point 63° at 760^{mm}.

$$V = 1 + 0{\cdot}0010382\,t^2 + 0{\cdot}0000017114\,t^2 + 0{\cdot}000000005447\,t^3\ (-7^0{\cdot}4 \text{ to } +60^0{\cdot}2)$$

Pierre's fourth paper(1), lastly, treats of the following liquids:

Sulphurous acid ($S\ O_2$). Spec. grav. 1·4911 at — 20°·5. Boiling point — 8° at 759^{mm}·2.

$$V = 1 + 0{\cdot}0014964\,t + 0{\cdot}0000223375\,t^2 - 0{\cdot}000000495759\,t^3\ (-25{\cdot}9 \text{ to } -9^0{\cdot}5)$$

this formula gives the volume for a temperature, which is d° higher than — 25°·85, the volume at the latter temperature = 1.

Sulphite of oxide of ethyl ($C_4\ H_5\ S\ O_3$). Spec. grav. 1·1063. Boiling point 160°·3 at 763^{mm}·8.

$$V = 1 + 0{\cdot}00099348\,t + 0{\cdot}0000010904\,t^2 + 0{\cdot}0000000015394\,t^3\ (0^0 \text{ to } 160^0{\cdot}1)$$

For most of these liquids Pierre has calculated tables, indicating their volume at different temperatures, the volume at 0°, at the boiling point, or at other temperatures, being = 1. We cite those referring to volumes at the boiling temperature. The annexed table gives the volume of a liquid at 5, 10, 15 . . . . ., generally—D°, below the boiling point, the volume at the latter being = 10000. For bisulphide of carbon, ether and formic ether, for which Pierre has not constructed any tables, we have calculated them on the basis of the boiling points and the formulæ of expansion, which he has given; for water, we refer to what has been stated above, (page 45.)

Along with his observations, and the formulæ of expansion resulting therefrom, Pierre has communicated some considerations respecting the irregularities in the expansion of the liquids investi-

(1) Ann. Ch. Phy. [3] XXI. 336; abstracted Ann. Ch. Pharm. LXIV, 177.

Expansion of liquid bodies by heat.

gated, and whether they can be employed in the construction of correct thermometers; farther a comparison of the average expansion for 1^0 during an elevation of temperature from 0^0 to t^0, (the average coefficient of expansion,) with the expansion during an elevation of temperature from t^0 to $(t + 1)^0$ (the true coefficient at t^0) (1). He compares, moreover, the changes of volume, exhibited by equal bulks of different liquids at their boiling points, when cooled an equal number of degrees below these boiling points; this comparison is contained in the annexed table. It deserves, however, to be noticed, that Pierre(2), misled by an error of calculation, considered the contractions of formic ether and of acetate of oxide of methyl, as different, (and hence a difference in the case of all isomeric liquids as probable,) whilst his observations, as well (compare table) as the experiments of H. Kopp, which will be quoted directly, leave no doubt respecting the equality of the contraction of these compounds. Lastly he points out that the specific volume of sulphite of oxide of ethyl ($C_4\ H_5\ S\ O_3 = C_4\ H_5\ O + S\ O_2$) at its boiling point exactly equals the sum of the specific volumes of ether ($C_4\ H_5\ O$) and of sulphurous acid (SO_2) at their boiling points.

H. Kopp(3) has published researches on the specific gravity, the expansion by heat, and the boiling point of several liquids. He first describes the construction of his thermometers and dilatometers, (thermometer-like instruments for determining the expansion of liquids,) the method and the calculation of the experiments on expansion, the determinations of the specific gravity, and of the boiling point; he then passes over to the investigation of 18 liquids, the preparation and analysis of which are communicated, and gives the results which he has obtained. The specific gravities are found for 0^0, and refer to water of the same temperature as unit. The boiling points are corrected for a barometric pressure of 760^{mm}, on the supposition that for small distances from the boiling point, the law of Dalton may be considered as correct, and according to Regnault's determination respecting the oscillations of the boiling point of water, with the changes of the barometer; with most substances the boiling point was observed both with the thermometer half immersed in the liquid and entirely surrounded by the vapour. We give here the latter observations. The following formulæ for expansion are (with the exceptions of those

(1) A synopsis of these results, important for thermometry in general, has been given by Pierre in Compt. Rend. XXVII, 213.

(2) Ann. Ch. Phys. [3] XV, 403.

(3) Pogg. Ann. LXXII, 1 and 223.

for water) the means of formulæ, which being derived from various series of observations, and with the application of various appa- ratus, had given very concordant results; they give the true volume V at a temperature t^0, the volume at $0^0 = 1$; we give here likewise in brackets the limits of temperature within which the experiments of expansion were instituted. Expansion by heat of solid bodies.

Water (HO); the expansion of water from 0^0 to 100^0 cannot be accurately represented by *one* formula; Kopp gives the following expressions for the temperatures:

$$0 \text{ to } 25^0 : V = 1 - 0{\cdot}000061045\,t + 0{\cdot}0000077183\,t^2 - 0{\cdot}00000003734\,t^3$$
$$25 \text{ „ } 50^0 : V = 1 - 0{\cdot}000065415\,t + 0{\cdot}0000077587\,t^2 - 0{\cdot}000000035408\,t^3$$
$$50 \text{ „ } 75^0 : V = 1 + 0{\cdot}00005916\,t + 0{\cdot}0000031849\,t^2 + 0{\cdot}0000000072848\,t^3$$
$$75 \text{ „ } 100^0 : V = 1 + 0{\cdot}00008645\,t + 0{\cdot}0000031892\,t^2 + 0{\cdot}0000000024487\,t^3$$

From the first of these formulæ, the temperature at which the water has its maximum density, is found to be $4^0{\cdot}08$.

Pyroxylic spirit (hydrated oxide of methyl; $C_2\,H_4\,O_2$). Spec. grav. 0·81796. Boiling point $65^0.5$.

$$V = 1 + 0{\cdot}00115135\,t - 0{\cdot}00000028046\,t^2 + 0{\cdot}000000027766\,t^3 \quad (0^0 \text{ to } 69^0{\cdot}0)$$

Alcohol (spirits of wine, hydrated oxide of ethyl; $C_4\,H_6\,O_2$). Spec. grav. 0·80950. Boiling point $78^0{\cdot}4$.

$$V = 1 + 0{\cdot}00104139\,t + 0{\cdot}0000007836\,t^2 + 0{\cdot}000000017618\,t^3 \quad (0^0 \text{ to } 79^0{\cdot}8)$$

Fusel-alcohol (potato-oil, hydrated oxide of amyl; $C_{10}\,H_{12}\,O_2$). Spec. grav. 0·8253. Boiling point $131^0{\cdot}1$.

$$V = 1 + 0{\cdot}00090692\,t + 0{\cdot}00000035970\,t^2 + 0{\cdot}000000013786\,t^3 \quad (11^0{\cdot}6 \text{ to } 130^0{\cdot}9)$$

Ether (oxide of ethyl; $C_4\,H_5\,O$ or $C_8\,H_{10}\,O_2$). Spec. grav. 0·73658. Boiling point $34^0{\cdot}9$.

$$V = 1 + 0{\cdot}00148026\,t + 0{\cdot}00000350316\,t^2 + 0{\cdot}000000027007\,t^3 \quad (0^0 \text{ to } 33^0{\cdot}0)$$

Aldehyde (hydrated oxide of acetyl; $C_4\,H_4\,O_2$). Spec. grav. 0·80092. Boiling point $20^0{\cdot}8$.

$$V = 1 + 0{\cdot}0015464\,t + 0{\cdot}0000069745\,t^2 \quad (0^0 \text{ to } 21^0{\cdot}2)$$

Acetone ($C_3\,H_3\,O$ or $C_6\,H_6\,O_2$). Spec. grav. 0·81440. Boiling point $56^0{\cdot}3$.

$$V = 1 + 0{\cdot}00134810\,t + 0{\cdot}0000026090\,t^2 + 0{\cdot}0000000115592\,t^3 \quad (0^0 \text{ to } 62^0{\cdot}2)$$

Benzole (benzine; $C_{12}\,H_6$). Spec. grav. 0·89911. Boiling point $80^0{\cdot}4$.

$$V = 1 + 0{\cdot}00117626\,t + 0{\cdot}00000127755\,t^2 + 0{\cdot}0000000080648\,t^3 \quad (11^0{\cdot}4 \text{ to } 81^0{\cdot}4)$$

Formic acid ($C_2\,H_2\,O_4$). Spec. grav. 1·2227. Boiling point $105^0{\cdot}3$.

$$V = 1 + 0{\cdot}00099269\,t + 0{\cdot}00000062514\,t^2 + 0{\cdot}0000000059650\,t^3 \quad (5^0\,4 \text{ to } 103^0{\cdot}5)$$

Expansion by heat of solid bodies.

Acetic acid ($C_4\ H_4\ O_4$). Spec. grav. 1·08005. Boiling point 117°·3.

$$V = 1 + 0{\cdot}00105703\ t + 0{\cdot}00000018323\ t^2 + 0{\cdot}0000000096435\ t^3\ (17^0{\cdot}7 \text{ to } 109^0{\cdot}6)$$

Butyric acid ($C_8\ H_8\ O_4$). Spec. grav. 0·98862. Boiling point 157°·0.

$$V = 1 + 0{\cdot}0010461\ t + 0{\cdot}00000056244\ t^2 + 0{\cdot}0000000054201\ t^3\ (12^0{\cdot}1 \text{ to } 141^0{\cdot}9)$$

Formiate of oxide of methyl ($C_4\ H_4\ O_4$). Spec. grav. 0·99840. Boiling point 33°·4.

$$V = 1 + 0{\cdot}0014055\ t + 0{\cdot}0000017131\ t^2 + 0{\cdot}000000045947\ t^3\ (0^0 \text{ to } 30^0{\cdot}9)$$

Formic ether (formiate of oxide of ethyl; $C_6\ H_6\ O_4$). Spec. grav. 0·94474. Boiling point 54°·9.

$$V = 1 + 0{\cdot}00136416\ t + 0{\cdot}00000013538\ t^2 + 0{\cdot}000000039248\ t^3\ (0^0 \text{ to } 63^0{\cdot}1)$$

Acetate of oxide of methyl ($C_6\ H_6\ O_4$). Spec. grav. 0·95620. Boiling point 56°·3.

$$V = 1 + 0{\cdot}0012779\ t + 0{\cdot}0000039171\ t^2 - 0{\cdot}000000003639\ t^3\ (0^0 \text{ to } 62^0{\cdot}3)$$

Acetic ether (acetate of oxide of ethyl; $C_8\ H_8\ O_4$). Spec. grav. 0·91046. Boiling point 74°·3.

$$V = 1 + 0{\cdot}0012738\ t + 0{\cdot}0000021914\ t^2 + 0{\cdot}000000011797\ t^3\ (0^0 \text{ to } 71^0{\cdot}8)$$

Butyrate of oxide of methyl ($C_{10}\ H_{10}\ O_4$). Spec. grav. 0·92098. Boiling point 95°·9.

$$V = 1 + 0{\cdot}00119565\ t + 0{\cdot}0000018103\ t^2 + 0{\cdot}0000000098292\ t^3\ (6^0{\cdot}9 \text{ to } 94^0{\cdot}6)$$

Butyric ether (butyrate of oxide of ethyl; $C_{12}\ H_{12}\ O_4$). Spec. grav. 0·90412. Boiling point 114°·8.

$$V = 1 + 0{\cdot}00117817\ t + 0{\cdot}0000013093\ t^2 + 0{\cdot}000000009560\ t^3\ (12^0{\cdot}0 \text{ to } 111^0{\cdot}1)$$

Valerianate of oxide of methyl ($C_{12}\ H_{12}\ O_4$). Spec. grav. 0·901525. Boiling point 116°·2.

$$V = 1 + 0{\cdot}00112115\ t + 0{\cdot}0000017044\ t^2 + 0{\cdot}0000000058627\ t^3\ (5^0{\cdot}5 \text{ to } 104^0{\cdot}1)$$

The results obtained with these formulæ are contained in the annexed table A, which indicates the volume of the liquids at 5, 10 . . . and generally at T° above 0, the volume at 0° = 1. Table B gives the contraction for equal thermal distances from the boiling points, and the volumes of the liquids at 5, 10 . . . . and generally D°, below their observed boiling points, their volumes being 1000° at these boiling points, which are once more indicated in the headings.

The expansion of several liquids has been examined also by Frankenheim(1); he availed himself of the same method (determination of the changes of volume in thermometer-like instruments), differing, however, in the details of application. The substances

(1) Pogg. Ann. LXXII, 422, with reference to a paper, ibid. 177.

investigated are not rigorously characterized as to their chemical composition. The following specific gravities refer to 0^0; V is the true volume for t^0 (according to experiments made between the temperatures indicated within brackets after each formula). Expansion by heat of solid bodies.

Oil of turpentine, which, though repeatedly distilled over chloride of calcium, had probably absorbed some water, and which disengaged a permanent gas, when subjected to ebullition. Spec. grav. 0·8902.

$$V = 1 + 0{\cdot}0008474\,t + 0{\cdot}000001248\,t^2 \; (11^0 \text{ to } 145^0)$$

Lemon oil, first specimen, (the same remarks as in the last case). Spec. grav. 0·8380.

$$V = 1 + 0{\cdot}0008660\,t + 0{\cdot}000001161\,t^2 \; (35^0 \text{ to } 133^0)$$

Lemon oil, second specimen, (the preceding one slightly changed by keeping). Spec. grav. 0·8661.

$$V = 1 + 0{\cdot}0007902\,t + 0{\cdot}000002053\,t^2 \; (15^0 \text{ to } 122^0)$$

Petroleum (preparation and composition similar to those of oil of turpentine). Spec. grav. 0·8467.

$$V = 1 + 0{\cdot}0008994\,t + 0{\cdot}000001396\,t^2 \; (24^0 \text{ to } 120^0)$$

Acetic ether, of a spec. grav. 0·9051.

$$V = 1 + 0{\cdot}001040\,t + 0{\cdot}00000363\,t^2 \; (13^0 \text{ to } 68^0)$$

Acetic acid (most likely dilute), of a spec. grav. 1·0522.

$$V = 1 + 0{\cdot}0004924\,t + 0{\cdot}00000513\,t^2 \; (13^0 \text{ to } 101^0)$$

Formic acid (dilute), of the spec. grav. 1·1051.

$$V = 1 + 0{\cdot}0005126\,t + 0{\cdot}000002721\,t^2 \; (15^0 \text{ to } 99^0)$$

Solution of chloride of zinc, of the spec. grav. 1·3632.

$$V = 1 + 0{\cdot}0005435\,t + 0{\cdot}000001320\,t^2 \; (15^0 \text{ to } 103^0)$$

Potassa solution, of the spec. grav. 1·2738.

$$V = 1 + 0{\cdot}0004150\,t + 0{\cdot}000000577\,t^2 \; (13^0 \text{ to } 101^0)$$

The volumes for different temperatures calculated by Frankenheim according to this formula, are synoptically arranged in the annexed table (also of a formic acid of 1·04405 spec. grav., for the expansion of which, however, no formula is given).

Maximum Density of Water.—Joule and Playfair(1) have determined the temperature, at which water is at its maximum density; they availed themselves, in a peculiar manner, of the principle, already used before for the same purpose, that in water not uniformly heated throughout its mass, those layers, the temperature of which approaches that of the maximum density, descend, while the others

(1) Phil. Mag. [3] XXX, 41; abstracted Pogg. Ann. LXXI, 574.

Maximum density of water.

ascend to replace them. Their apparatus consisted of two upright vessels ($4\frac{1}{2}$ feet high, and 6 inches in diameter) connected with each other at the top by means of a trough, at the bottom by means of a tube, furnished with a stopcock, whilst the current in the trough could be stopped by a slide. The communication of the two vessels being interrupted, they were filled, the one with water of about $2^0 \cdot 8$, the other with water of about $5^0 \cdot 3$; after immersing accurate thermometers into both vessels, the communication was reopened, (the temperature of the surrounding atmosphere during these experiments being from 3·3 to 5^0). A current was thus established, passing through the bottom tube from the vessel with the denser water to the vessel containing the water of inferior density, and in the opposite direction through the trough at the top; this current was observed by means of a glass ball floating upon the water in the trough, the motion of which, as to direction and velocity, was carefully ascertained. Changes in density for equal thermal intervals, above and below the temperature of the maximum density, could be considered as equal within these narrow limits. The direction of the current in the top-trough was from the vessel, whose temperature differed most from that of the maximum density, to the vessel whose temperature differed less from it; no current would have been perceptible, if the temperature of the water in both vessels had equally differed from that of the maximum density, or if the temperature sought had been found to be the arithmetical means of the original temperatures. The latter was deduced from the observations by interpolation; the mean of the results of different sets of experiments, well according with each other, was found to be $3^0 \cdot 945$.

Expansion of Mercury.—Regnault(1) has instituted numerous experiments respecting the absolute expansion of mercury. He determined it by measuring the difference of pressure, exerted by mercurial columns of equal height, but unequal temperatures. It is impossible to give a detailed account of his method without drawings. The volume of the mercury at 0^0 being equal to 1, his determination gives it for t^0 of the air thermometer:

$$1 + 0 \cdot 000179007t + 0 \cdot 0000000252316t^2,$$

And hence, at	$50^0 = 1 \cdot 009013$	at $150^0 = 0 \cdot 027419$	at $250^0 = 0 \cdot 046329$
„	$100^0 = 1 \cdot 018153$	„ $200^0 = 0 \cdot 036811$	„ $300^0 = 0 \cdot 055973$
			$350^0 = 0 \cdot 065743$

(1) Relation des expériences entreprises —— pour déterminer les principales lois physiques et les données numériques qui entrent dans le calcul des machines à vapeur, Paris 1847, 271.

Expansion of mercury.

With the aid of Regnault's determination of the expansion of mercury, Izarn(1) has calculated tables for the reduction to 0^0 of the barometric column.

Specific Heat; Fusion; Latent Fusion-Heat.—A note, by Rudberg(2), on the quantities of heat in mixtures of metals at their fusing point, has been published, which this physicist had communicated to Poggendorff in 1839.

Quantities of Heat in metallic Mixtures.—Rudberg considered it probable, that in an alloy of two metals, which would cool regularly, (that is, in which one portion of the metal would not solidify on cooling, before the remainder, which would be indicated by the thermometer becoming twice stationary), or in other words, in a chemical alloy, each of the two metals contains the same amount of heat between the fusing point of the alloy and its own fusing point. Assuming the specific heat of a metal to be constant, this view is expressed by the following formula:

$$M' c' (T' - T) = M'' c'' (T'' - T).$$

(M' and M'' representing the weights of the metals, c' and c'' their specific heats, T' and T'' their fusing points, and T the fusing point of the alloy).

Taking Dulong's law of the inverse proportion existing between specific heat and atomic weight as strictly correct, and the ratio $M' : M''$ of the weights of the two metals, as represented by the atomic ratio 1 : n, the above formula becomes

$$T' - T = n (T'' - T).$$

Several experiments are quoted by Rudberg in confirmation of his view, some of which indeed approximately correspond with it. (In calculating the formula for the bismuth-compounds, the new atomic weight of this metal, agreeing with Dulong's law, has been adopted.

The following fusing points were obtained by Rudberg:

For Sn = 228°·5	Pb = 326°·0	Sn = 228°·5	Bi = 268°·3	Sn = 228°·5	Cd = 320°·0
Sn_3Pb = 182·5	182·5	Sn_3Bi_2 = 136·4	136·4	Sn_2Cd = 173·8	173·8
46·0	143·5	92·1	131·9	54·7	146·2
3 . 46·0 =	138·0	3 . 92·1 =	276·3	2 . 54·7 =	109·4
		2 . 131·9 =	263·8		

(1) Millon et Reiset's Annuaire de chimie, 1848, 498.
(2) Pogg. Ann. LXXI, 160; Ann. Ch. Pharm. LXIV, 183.

Quantities of heat in metallic mixtures.

Bi = 268°·3	Cd = 320°·0	Bi = 268°·3	Pb = 326°·0
Bi Cd = 146 ·3	146 ·3	$Bi_4\ Pb_3$ = 125 ·3	125 ·3
122 ·0	173 ·7	143 ·0	200 ·7
		4 . 143 ·0 =	572 ·0
		3 . 200 ·7 =	602 ·1

The results, with the exception of those obtained with alloys of cadmium, are approximately concordant. Rudberg seems to have been of opinion, that the atomic weight of cadmium, generally adopted, not agreeing with Dulong's law, a correction would produce corresponding results; this, however, is not the case.

Rudberg conjectured, that in ternary alloys, the sum of the quantities of heat in the more electro-positive metals equalled the quantity of heat in the more electro-negative metal. The fusing points of an alloy $Zn\ Pb_2\ Sn_2$ examined by Svanberg and of its constituents are as follows:

Zn =	400°·0	Pb = 326°·0	Sn = 228°·5
$Zn\ Pb_2\ Sn_2$ =	168 ·0	168 ·0	168 ·0
	232 ·0	158 ·0	60 ·5

232·0 + 2 . 158·0 = 548·0
9 . 60·5 = 544·5

On specific Heat, Fusing Point, and latent Fusion-Heat.—Person has published researches on the specific heat of various bodies in the solid and fluid states, on their latent fusion-heat, and on the connection between these properties; his observations are contained in short notes, and in more detailed communications, which have both to be discussed: the statements made therein not being always in accordance with each other.

In his earlier publications(1), he communicated the following results of his investigations. T represents the fusing point, L the latent fusion heat of the unit of weight; in the third column the temperatures are given, between which the specific heat W was determined.

(1) Compt. Rend. XXIII, 162; Instit. 1846, 247; Pogg. Ann. LXX, 300; Compt. Rend. XXIII, 336; Instit. 1846, 277; Pogg. Ann. LXX, 302; Ann. Ch. Pharm. LXIV, 179.

On specific heat, fusing point and latent fusion-heat.

Substance.	T	L		W
Tin	235°C	14·3	340° and 240°	0·061
Bismuth	270	12.4	370 „ 280	0·035
Lead	332	5·15	440 „ 340	0·039
Alloy $Pb_2 Sn_2 Bi_4$	96	5·96	300 „ 136	0·036
Ditto	—	—	136 „ 107	0·047
Ditto	—	—	80 „ 14	0·060
Ditto	—	—	50 „ 12	0·049
Alloy $Pb\ Sn_2\ Bi$	145	7·63	330 „ 143	0·046
Phosphorus	44·2	4·71	100 „ 50	0·212
Sulphur	115	9·175	147 „ 120	0·235
Nitrate of soda	310·5	62·98	430 „ 330	0·413
„ „ potassa	339	46·18	435 „ 350	0·344
Phosphate of soda ($PO_5,2NaO,25HO$)	36·4	54·65	79 „ 44	0·758
Ditto	—	—	2 „— 20	0·454
Chloride of calcium ($Ca\ Cl + 6\ HO$)	28·5	45·79	127 „ 100	0·519
Ditto	—	—	100 „ 60	0·628
Ditto	—	—	60 „ 31	0·358
Ditto	—	—	28 „ 4	0·647
Ditto	—	—	2 „— 20	0·406
Bees'-wax (yellow)	62·0	43·51	102 „ 66	0·54
Ditto	—	—	58 „ 42	0·72
Ditto	—	—	42 „ 26	0·79
Ditto	—	—	26 „ 6	0·52
Ditto	—	—	2 „— 20	0·39
Ice	—	—	0 „— 30	0·505
Zinc	423	27·46		

Person expresses the connection between the fusing point, the specific heat of the body in the solid and liquid state, and the latent heat by the following formula:

$$(160 + T)\,d = L$$

T and L having the above meaning, and d representing the difference of the specific heat of the body in the solid and liquid state; he asserts, that in order to obtain the latent heat, the difference of the two specific heats has to be multiplied by the number of degrees between — 160° and the fusing point. From the data given in the foregoing table, and with the aid of the specific heats, as determined by Regnault, he calculates the following numbers as representing the latent heat of various substances, with which calculated values he compares the results obtained by observation.

Substance.	Calculated.	Observed	Substance.	Calculated.	Observed.
Water	79·20	79·25	Sulphur.	9·08	9·18
Chloride of calcium.	43 60	45·79	Nitrate of soda	63·52	62·98
Phosphate of soda	59·70	54·65	„ „ potassa	52·39	46·18
Phosphorus	4·76	4·71			

On specific heat, fusing point and latent fusion-heat.

With several other bodies, the calculated and observed numbers do not accord so well in favour of the formula. Person endeavours to account for these discrepancies.—He found the specific heat of wax in the solid state, when nearly approaching its fusing point, to be greater than in the liquid state, so that, taking the numbers thus obtained as a basis, the formula would lead to an absurdity, L becoming negative. At a greater distance however from the fusing point, he found the specific heat of wax to be much smaller (0·39); he therefore considers, that whatever is found above 0·39 should be considered as latent heat, (heat becoming latent before fusion, heat consumed in softening), and consequently be deducted from the specific heat as found between 2^0 and 60^0; the formula would then become applicable. Again the formula does not apply to metals, their specific heats in the solid and liquid state being nearly equal, and, consequently, d becoming = 0. Person, before attempting an explanation of this circumstance, considers his formula from a different point of view. If the specific heats of the body, in the solid and liquid state, be represented by c and C, $(160+T)\,c$ represents the amount of heat contained in the weight unit of the solid body between -160^0 and T^0; by adding the latent heat L, the amount of heat contained in the same quantity of the body in the liquid state, within the same limits, is found to be $(160 + T)\,c + L$. The above formula $(160 + T)\,d = L$, by introducing $C - c$ instead of d, may also be written thus:

$$(160 + T)\,c + L = (160 + T)\,C,$$

i. e. the amount of heat which must be removed from a fluid mass, in order to cool it down to -160^0, can be calculated, without considering that its state of aggregation alters, just as though the mass remained fluid.

He quotes the fact, that several bodies are capable of remaining liquid even below their fusing points, and is of opinion that the fluid state of a body may be reconciled with the lowest temperatures, and that solidification is merely accidental.—He then proposes, in the formula already cited, which appears to be inapplicable to metals, to represent the specific heat of the body in the liquid state by the number found *below* the fusing point, instead of that observed *above* it. Though these numbers were concordant in many cases, especially in the case of bodies easily retaining their liquidity below the fusing point, this was not the case with metals. The incorrectness of the formula was, therefore, by no means proved by its inapplicability to metals, inasmuch as the true values of the specific heat in the liquid state did

not admit of being introduced. The specific heat of metals below the fusing point might be greater in the liquid than in the solid state. (Here it must be observed, that it should likewise be greater than the specific heat of metals, in the liquid state, above the fusing point, which is improbable. Again, in treating even of several non-metallic substances, the experimental number introduced into the formula for C, had been obtained for temperatures *above* the fusing point, while nothing proves this number to agree with the specific heat of the substance in the liquid state *below* the fusing point).

On specific heat, fusing point and latent fusion-heat.

Person draws some farther conclusions from his experiments and formulæ.—The heat required for the fusion of metals was proportionate to the force necessary to separate their particles, as might be seen by comparing the fusion-heats with the coefficients of elasticity, or with the measures of cohesion.

The absolute zero was at — 160°.—Latent heat was the difference of heats contained in the solid and liquid body at the temperatures T of solidification. Representing the distance of the usual (arbitrary) zero, from the absolute zero by x°, the former was = (x + T) c, the latter = (x + T) C, the latent heat = (x + T) (C—c). Experience showed x to be = 160. The latent fusion-heat was probably a variable magnitude, changing with the temperatures at which the bodies pass from the one state of aggregation to the other, and diminishing with the decrease of these temperatures.

With the assistance of this latter view, Person has endeavoured to solve a problem concerning the fusion of alloys(1). He found the latent fusion-heat of an alloy of 8 parts of bismuth, 5 of lead, and 3 of tin, (corresponding to $Bi_3\ Pb_2\ Sn_2$), solidifying at 96°, to be = 6; by calculating, however, from the latent heats of the constituents, as given in the foregoing table, we arrive at the number 10·4. Person accounts for this difference by the circumstance of the latent heats of the constituents having been introduced into calculation as found for higher temperatures, (the fusing points of the individual metals,) whereas they should have been taken at 96°, at which temperature the metals liquify in the alloy, and have an inferior latent heat. Direct observation being impossible in this case, the latter is calculated in the following manner. In the formula (160 + t) d = L, originally (page 55) constructed only for a case in which t represented the fusing point in the common acceptation of the term—he assumes t to represent generally a temperature

(1) Compt. Rend. XXIII, 626; Instit. 1846, 325; Pogg. Ann. LXX, 388; Ann. Ch. Pharm. LXIV, 181.

On specific heat, fusing point and latent fusion-heat.

at which the substance may be solid or liquid, (or the latter may be imagined). For t = the fusing point, t and L being known, d, the difference of the specific heats in the solid and liquid state below the fusing point may now be calculated for each metal. Assuming d to be known, (and to be constant for every metal,) he now finds, for every other temperature, the amount of latent heat L belonging to it. Thus he obtains for 96°, with tin L = 9·3, with bismuth L = 7·382 and with lead L = 2·7, numbers certainly differing considerably from those obtained for higher temperatures, (the ordinary fusing points,) from which, however, the latent heat of the above mixture is found to be 6·3, very nearly coinciding with direct observation.—The latent heat of the alloy $Pb\ Sn_2\ Bi$ (fusing at 145°) when calculated upon exactly the same principle, was found to amount to 7·85, direct experiment giving 7·63.

According to Person, the latent fusion-heat of mercury is 2·82(1), the fusing point of cadmium 320°·7, (air thermometer) and its latent fusion-heat 13·58; that of silver was found, (with less certainty) to be 21·07(2).

In a later publication on latent fusion-heat(3), Person endeavours to give further arguments in favour of the formula quoted, and of the deductions drawn from it. In this paper, he communicates the investigation of fewer substances than those specified in his former publications; entering, however, into a more accurate description of all the details of experiment. He first describes the calorimeter, employed in the determination of the latent and specific heat, (he operated by the method of mixture,) and discusses the corrections which the direct experimental numbers require; he then communicates the results obtained with five different substances.

He ascertained the specific heat of ice by determining the decrease in temperature, which ice, cooled down to about —20°, produced without melting, in a liquid. He found 0·5070, as the average of several very concordant experiments, in some of which oil of turpentine, (specific heat at about 0°=0·416°,) in others a solution of sea salt, (100 parts of water containing 6·75 parts of chloride of sodium, specific heat 0·95,) was employed. He ascertained the same value by measuring the decrease of temperature produced in water by ice when allowed

(1) Compt. Rend. XXV, 334; Pogg. Ann. LXXIII, 469; Ann. Ch. Phys. [3] XXIV, 257; Ann. Ch. Pharm. LXVIII, 180.

(2) Compt. Rend. XXVII, 258; Arch. Ph. Nat. IX, 135; Pogg. Ann. LXXV, 460; detailed in Ann. Ch. Phys. [3] XXIV, 265.

(3) Ann. Ch. Phys. [3] XXI, 295; Pogg. Ann. LXXIV, 109 and 509.

to melt, (correction of course being made in the calculation for the latent fusion-heat of ice, which was assumed to be known). The average of several experiments gave the number 0·5057 as the specific heat of ice; the mean of the numbers obtained by the two methods(1) being therefore 0·504. By substituting this number for c in the formula $(x + T) . (C - c) = L$ (see page 57), Person calculates the value of x; the other magnitudes in the case of water being known, namely, $T = 0$, $C = 1$, $L = 79·25$.—The latent fusion-heat was variable. The weight-unit of water at 0°, on freezing, liberated 79·15 units of heat. Five heat-units (the specific heat of ice being 0·5) were required to raise the temperature of the weight-unit of ice from — 10° to 0°, and 79·2 heat-units to melt it. The weight-unit of ice at—10°, when melting into water of 0°, absorbed, therefore, altogether 84·2 heat-units, and, vice versâ, the same amount of heat had to be abstracted in the reconversion of water at that temperature into ice of — 10°. Supposing water of 0° to be cooled down to — 10° without solidifying, it lost 10 units of heat, and when now suddenly converted into ice, it could lose no more than 84·2 — 10 = 74·2 units of heat; this was, therefore, the latent heat of liquid water at — 10°, a value considerably differing from that at 0°. The variation of the latent heat, with the temperature T, for which a change in the state of aggregation is assumed, is expressed by the formula that has been repeatedly quoted. The specific heat of water, liquid below 0°, was just now assumed to be = 1. Person has convinced himself that the cooling of water, passing without solidification, from a temperature above 0° to a temperature below 0°, takes place regularly, and without the sudden change in the relation between time and intensity of cooling, that would be occasioned by a change in the specific heat.

On specific heat, fusing point and latent fusion-heat.

According to Person, the specific heat of solid phosphorus between 7° and — 21° is 0·1788 (Regnault states it to be 0·1887 between 10° and 30°), the fusing point is = 44·2°, its specific heat in the fluid state is = 0·2045, its latent fusion-heat = 5·0. He estimates the latter at 5·2, by a calculation based on later determinations.

The fusing point of sulphur, not over-fused by too much heating, was found to be 115°, the specific heat of liquid sulphur, between

(1) A third method of ascertaining the specific heat of ice from the weight of ice deposited upon a known amount previously cooled below 0°, when introduced into water at 0°, has been tried by Clément and Désormes; Person found this method inapplicable, as the quantity of ice, far from being definite, augments with the time during which the cooled ice is left immersed.

On specific heat, fusing point and latent fusion-heat.

120^0 and 150^0, = 0·234; the latent fusion-heat = 9·37. His formula gives for the latter 9·35, (the specific heat of sulphur being taken as 0·2).

He found the fusing point of nitrate of soda to be $310^0{\cdot}5$; its specific heat in the fluid state, between 430^0 and 320^0, = 0·413; the latent fusion-heat = 62·975. According to his formula, it is 63·4, the specific heat of solid nitrate of soda having been taken at 0·27821, according to Regnault's determination.

For nitrate of potassa, he found the fusing point to be 339^0; its specific heat in the fluid state, between 350^0 and 435^0, = 0·33186; its latent fusion-heat = 47·371; calculated by his formula the latter is 46·462 (the specific heat of solid nitrate of potassa being taken at 0·23875 according to Regnault).

Person now discusses some farther inferences from his formula, which we have already pointed out, and promises to develope more fully, in another communication, his assertion that bodies cease to contain heat at a temperature of 160^0 below zero.

In this memoir(1) he first quotes the fact, that the relation of the quantities of heat, contained in different bodies at the same temperature, is given approximately by the ratio of their specific heats; this would indeed be accurately thus expressed, if the relation of the specific heats among themselves was constant. If, in addition to the ratio existing between the total amounts of heat in two bodies, the difference of these quantities be likewise known, the former values may be calculated. In representing by x and x^1 the absolute quantities of heat contained in the weight-units of ice and water at 0^0, their ratio is $\frac{x}{x^1} = \frac{0{\cdot}504}{1}$ (0·504 being the specific heat of ice) and their difference $x^1 - x = 79{\cdot}2$ (the latent fusion-heat of water); from this we find x to be = 80 and $x^1 = 160$, *i. e.* the quantity of heat existing in each of these bodies is = 160 times the specific heat, or, their total amount of heat is expelled by lowering their temperature to -160^0. Hence -160^0 must be the absolute point of zero.

Person then proceeds to communicate the details of his experiments with metals. His results differ somewhat from his former statements, (see page 54); they are as follows, (the numbers of Regnault being taken for the specific heats in the solid and fluid states, and the last column denoting the limits of temperatures between which the specific heat of the substances in the liquid state holds good).

(1) Ann. Ch. Phys. [3] XXIV, 129.

On specific heat, fusing point and latent fusion-heat.

Metal.	Fusing point by the mercury- thermometer.	air- thermometer.	Specific heat in the solid state.	liquid state.	Latent fusion-heat.	
Tin . . .	235°·0	232°·7	0·0562	0·0637	14·252	250° and 350°
Bismuth . .	270 ·5	266 ·8	0·0308	0·0363	12·640	280 „ 380
Lead . . .	334 ·0	326 ·2	0·0314	0·0402	5·369	350 „ 450
Zinc . . .	433 ·3	415 ·3	0·0956	—	28·130	

The specific heat of metals in the liquid state is certainly greater than that of metals when solid, in no greater ratio, however, than that which Dulong found for the increase in the specific heat of metals remaining solid at high temperatures, so that no increment of the specific heat can be ascribed to the transit from the solid to the fluid state. Person treats this point in accordance with the views previously communicated by him, (page 56) and adds, that in the case of metals, the absence of any such increase in the specific heat, so perceptible in the liquefaction of water, sulphur, and salts, was probably due to their liquidity being imperfect compared with that exhibited by the former bodies.

He then discusses the determination of latent fusion-heat, and of the specific heat at higher temperatures, by means of the method of cooling, to which he sometimes resorted, most of his determinations being conducted according to the method of mixture.

Then follows the exact statement of his experiments on the specific heat of liquid alloys. In the following table, the final results (C) obtained for about 220° are given. Person calls attention to the following,—if the specific heat of an alloy be calculated from the specific heats of the constituents in the solid and liquid state, the results obtained in the former case being k, and in the latter K, then $\frac{k + K}{2}$ is found nearly equal to C. The calculation of k refers to a temperature as far below 220°, as that for which K has been determined is above this point; from this the conclusion might be drawn, that the specific heats of liquid alloys, and of the individual metals contained therein (considering them as a mixture—as distinguished from the real alloys) were equal at the same temperatures.

Alloy.	k.	K.	½ (k + K).	C.
$Bi_3 Pb_2 Sn_2$ . .	0·03560	0·04256	0·03908	0·03895
$Bi_2 Pb Sn_2$ . .	0·03785	0·04447	0·04116	0·04219
$Bi_3 Pb_2$ . . .	0·03106	0·03784	0·03444	0·03503
$Bi_3 Sn_4$ . . .	0·04150	0·04792	0·04447·	0·04540

According to Person the mixing of fused metals is attended by

On specific heat, fusing point and latent fusion-heat.

an increase of temperature; on introducing into melted lead a glass tube which contained bismuth in the fluid state, he found that if a rapid mixture of the metals was effected by breaking the tube, the temperature rose 30°. Person does not believe this elimination of heat to be a chemical effect; he is of opinion, that less heat is contained in an alloy in the liquid state, than in the separate constituents when liquid at the same temperature. According to Person's determination, the accession of 15·748 units of heat is necessary to raise the temperature of the unit of weight of $Pb_2 Bi_3$ from 20° to 330°, whereas to produce the same effect with a corresponding quantity of the constituents in a separate state, 19·570 would be required. The difference of heat was liberated in the transition of the metals into the alloy. With other alloys, (as those of bismuth with lead and tin, particularly bismuth with tin,) the above difference is found to be less, and observation exhibited an increase of temperature correspondingly inferior. Person concludes further, that the latent fusion-heat of alloyed metals is smaller than that of the metals in the separate state.

He demonstrates, moreover, that a decomposition takes place after the solidification of such alloys as have no point of separation, (as first observed by Rudberg), or in other words, in which none of the constituents become solid before another, *one* definite point of solidification being exhibited(1). The alloy $Bi_3 Pb_2 Sn_2$, once solidified, will quietly cool down to 57°, when the thermometer becomes stationary, or even rises, while the alloy expands, bursting the vessel in which it is contained, if made of glass or thin metal. An alloy, when poured into water, exhibits this development of heat at a lower temperature, it may then however amount to about 30° or more. The alloy solidified after fusion contains, a few degrees below the point of solidification (before the evolution of heat), a larger amount of caloric than when heated again to the same temperature after having been allowed to cool down perfectly (after the evolution of heat); in the same manner experiment gives a higher specific heat in the former than in the latter case. Of the experiments enumerated in the following table, the first was made with the alloy $Bi_3 Pb_2 Sn_2$, under the former circumstance, during the others the same alloy was in the latter condition. (Fusing point of the alloy 96°). These experiments show, however, that on warming the alloy a certain amount of heat becomes latent even below the

(1) Preliminary notice on this subject, Compt. Rend. XXV, 444; Pogg. Ann. LXXIII, 472.

fusing point, very likely in consequence of the combination of the products of separation, which are eliminated during cooling at lower temperatures. T expresses the fusing point, c the specific heat, Δ the thermometric interval in which it was determined, k the specific heat, as calculated from that of the constituents; c and k coincide for considerable distances from the fusing point. On specific heat, fusing point and latent fusion-heat.

Alloy.	Δ	c	Alloy.	T	Δ	c	k
$Bi_3\,Pb_2\,Sn_2$.	95° and 25°	0·1054	$Bi_3\,Pb_2$ . .	122°·4	99° and 17°	0·0317	0·0311
„	95 „ 23	0·0710	„	„	99 „ 16	0·0316	„
„	94 „ 22	0·0690	$Bi_3\,Sn_4$ . .	135·3	99 „ 17	0·0450	0·0415
„	82 „ 14	0·0598	Bi Pb Sn_2 .	145 ?	53 „ 17	0·0429	0·0401
„	51 „ 19	0·0374	„	„	51 „ 19	0·0417	„
„	51 „ 12	0·0377					

Person has farther endeavoured to find the latent fusion-heat of some alloys, as well as the amount of heat liberated during decomposition after solidification. He finds:

For Bi_3, Pb_2 Sn_2 the former = 4·50, the latter = 3·15
„ Bi_2, Pb, Sn_2 „ = 4·69, „ = 2·80

He concludes this memoir, by commenting on the view taken by Rudberg (see page 53) of the connection existing between the fusing points of alloys and those of their components. He does not make allowance for the circumstance, that in Rudberg's time, the atomic weight almost universally adopted for bismuth, was different from the present one, and that, consequently, the composition of the bismuth alloys, expressed in Rudberg's formulæ differ from that which he assigns to them. The remark that Rudberg had overlooked certain properties of some alloys is hence unfounded. Person's observations contain, however, several confirmations of Rudberg's view. Determinations made by the former gave the following fusing points:

Of Bi=266°·8	Sn=232°·7		Sn=232°·7	Pb=326°·2		Bi=266°·8	Pb=326°·2
$B_3\,Sn_4$=135 ·3	135 ·3		Sn_3Pb=182 ·8	182 ·8		$Bi_3\,Pb_2$=122 ·4	122 ·4
131 ·5	97 ·4		49 ·9	143 ·4		144 ·4	203 ·8
3 . 131 ·5 =	394 ·5		3 . 49 ·9 =	149 ·7		3 . 144 ·4 =	433 ·2
4 . 97 ·4 =	389 ·6					2 . 203 ·8 =	407 ·6

Person's results, which appear as the second terms in this conspectus, exhibit even in details a close coincidence with Rudberg's statements respecting the same substances.

Fusing point, specific heat, and latent heat, of phosphorus.

Fusing point, specific Heat, and latent Heat, of Phosphorus.—Desains(1) found the fusing point of phosphorus to be 44°·2; by observing the time necessary for the cooling of solid and fused phosphorus (remaining liquid below the fusing point), he considers the specific heat of this body to be the same in both states, (in contradiction to Person see page 59), and finds it, by the method of cooling, to be 0·2. He determined the latent fusion-heat, by ascertaining the increase of temperature exhibited in the solidification of liquid phosphorus, cooled down below the fusing point; he thus found it to be 5·4, and by the method of mixture it was found = 5·06.

Specific Heat of Compounds.—Woestyn(2), (unacquainted with the earlier researches of Schröder)(3), has studied the connection between the specific heat of compounds, and that of their constituents. Assuming A to represent the atomic weight, and C the specific heat of a compound, a_1, a_2, a_3 .... the atomic weight(4), c_1, c_2, c_3 .... the specific heat of the constituents of the compound, and n_1, n_2, n_3 .... figures denoting the number of atoms of each element contained in an atom of the compound, he proposes the following law,

$$AC = n_1 a_1 c_1 + n_2 a_2 c_2 + n_3 a_3 c_3 \dots$$

To establish his formula, he compares the values of A C, calculated for several compounds and alloys, with those empirically found, (the results obtained by Regnault being taken as the basis). It follows from this law that if the formulæ and the values for A C of several compounds be deducted from each other, whenever the differences of the formulæ are equal, the corresponding values of A C will likewise be equal. Finally, with the aid of this law as a basis, the product of the specific heat with the atomic weight for one of the components of any compound, may be found, if the corresponding product be known for the compound itself and the other components. The calculations communicated by Woestyn for the elaboration of the law and his conclusions, gave results corresponding very satisfactorily both with observation, and among themselves.

(1) Compt. Rend. XXIII, 149; Instit. 1846, 247; Arch. Ph. Nat. II, 409; Ann. Ch. Phys. [3] XXII, 432; Pogg. Ann. LXX, 315.

(2) Ann. Ch. Phys. [3] XXIII, 295; Pogg. Ann. LXXVI, 129; abstract Ann. Ch. Pharm. LXVIII, 175.

(3) Pogg. Ann. LII, 269.

(4) Woestyn assumes the atomic weight of several elements (Sb, Bi, Ag, K, Na, Cl, Br, I, N) to be equal to half their equivalents, an assumption also made by Regnault in his researches on specific heat.

Specific Heat of Water at different Temperatures.—Regnault(1) has determined very accurately the specific heat of water at various temperatures. His results show, that the quantity of heat, Q, which is lost by 1 weight-unit of water when cooled from T^0 to 0^0, expressed in units of heat, is

Specific heat of water at different temperatures.

$$Q = T + 0{\cdot}00002\, T^2 + 0{\cdot}0000003\, T^3$$

and the specific heat C of water at T^0

$$C = 1 + 0{\cdot}00004\, T + 0{\cdot}0000009\, T^2$$

according to which formulæ the following numbers were obtained:

T.	Q.	C.	T.	Q.	C	T.	Q.	C.
0°	0·000	1·0000	100°	100·500	1·0130	200°	203·200	1·0440
50	50·087	1·0042	150	151·462	1·0262	230	234·708	1·0568

Specific Heat of different Fluids.—H. Kopp(2) has determined the specific heat of the following liquids. (The third column indicates the thermometric interval in which the determinations were made).

Mercury	0·0332	44° to 24	Formic ether	0·513	39° to 20°
Pyroxylic spirit	0·645	43 „ 23	Acetate of methyl	0·507	41 „ 21
Alcohol	0·615	43 „ 23	Acetic ether	0·496	45 „ 21
Fusel-oil	0·564	44 „ 26	Butyrate of methyl	0·487	45 „ 21
Formic acid	0·536	45 „ 21	Valerianate of methyl	0·491	45 „ 21
Acetic acid	0·509	45 „ 24	Acetone	0·530	41 „ 20
Butyric acid	0·503	45 „ 21	Benzole	0·450	46 „ 19
Sulphuric acid	0·343	46 „ 21	Oil of mustard	0·432	48 „ 23

Andrews(3) determined the specific heat of bromine between 45^0 and 11^0, to be 0·107.

Specific Heat of Gases.—Favre and Silbermann(4) have described an apparatus for determining the specific heat of gases under different pressures. They will communicate hereafter the results obtained.

Boiling. Latent Vapour-heat of Water.—Regnault(5) has made extensive experiments on the latent heat of steam, and particularly on its quantity in saturated steam generated under different pressures.

(1) Relation, &c. (see p. 52), 729.
(2) Pogg. Ann. LXXV, 98; Ann. Ch. Pharm. LXVIII, 177 (in abstract).
(3) Chem. Soc. Quart. J. I, 18; Pogg. Ann. LXXV, 335.
(4) Compt. Rend. XXVII, 56.
(5) Relation &c. (see p. 92), 635 and 748.

Boiling. Latent vapour-heat of water.

Two different views had been previously proposed respecting this subject. Watt maintained, that the quantity of heat necessary for the conversion of a weight-unit of water at 0^0 into vapour, was subject to no change, whatever the pressure under which it was generated, *i. e.* that the sum of the latent heat and the heat indicated by the thermometer, in saturated steam, was constant. Southern, on the contrary, asserted that this sum varied according to the temperature, inasmuch as it was expressed by the heat of steam indicated by the thermometer (its temperature) and its latent heat, the latter being constant. Thus, according to Watt, the total amount of heat contained at any temperature in saturated steam is constant, according to Southern only the latent heat is so.

Regnault found, that experiment confirmed neither the one nor the other of these views. His results showed, that the weight-unit of saturated steam of T^0, contained a quantity of heat exceeding that of the weight-unit of water of 0^0, by $\lambda = 606{\cdot}5 + 0{\cdot}305\ T$, expressed in heat-units. By deducting from λ the difference of the amounts of heat contained in the weight-unit of water at T^0 and at 0^0 (values more accurately known since Regnault's researches on the specific heat of water at different temperatures), we obtain L, the latent vapour-heat of water at T^0. The following are, according to Regnault's determinations, the values of λ and L for saturated steam of the temperature T, and the corresponding elasticity, E, expressed in millimetres and atmospheres:

T.	E.		λ.	L.	T.	E.		λ	L.
	mm.	atm.				mm.	atm.		
0⁰	4·60	0·006	606·5	606·5	150⁰	3581·23	4·712	652·2	500·7
50	91·98	0·121	621·7	571·6	200	11688·96	15·3[illegible]0	667·5	464·3
100	760·00	1·000	637·0	536·5	230	20926·40	27·535	676·6	441·9

Considerations, particularly from the theoretical and mathematical point of view, respecting latent vapour-heat have been communicated by Pouillet(1), who endeavours to establish a connection between his views and the experiments of former inquirers. An abstract of this memoir cannot well be given, the same applies to a note on the heat of vapours by Lubbock(2). We limit ourselves to pointing out, that Pouillet also arrives at the result, that the higher the temperature of saturated

(1) Compt. Rend. XXIV, 915; Pogg. Ann. Ergänzungs, Bd. II, 579.
(2) Phil. Mag. [3] XXXI, 90.

steam, the larger the total amount of heat, and the smaller that of latent heat; that, with carbonic acid vapour, on the contrary, the total amount of heat diminishes with increasing temperatures, and that the same deportment is exhibited by the vapour of condensed protoxide of nitrogen. He found the latent heat of steam at 0^0 to be = 560^0 (differing considerably from Regnault's more accurate determinations). **Boiling. Latent vapour-heat of water.**

Latent Vapour-Heat of different Bodies.—Andrews(1) has examined various liquids as to latent vapour-heat, and several other properties. The fluid under examination was heated to ebullition in a small flask, the neck of which was connected with a receiver having a vertical serpentine tube, both of glass, and immersed in water. The increase of temperature of the latter having been observed, the quantity of vapour which had given rise to this increase was determined by weighing the receiver before and after the experiment. A screen protected the vessel of water from being heated by radiation from the flask; the necessary corrections for the loss of heat sustained by the water during the experiment were also attended to.—Andrews observed the boiling points whilst the thermometers were in the vapour.—The specific heat was determined, by rapidly pouring the heated liquid into a small glass tube immersed in water, noting its increase of temperature, ascertaining the weight of the fluid poured into the tube, &c. He obtained the following results:

Substance.	Latent heat.		Boiling point.	Specific heat.
	A	B		
Water	535·9	318·3	100^0 at 760^{mm}	1·000
Alcohol	202·4	324·2	77 ·9 „ 760	0·617
Bromine	45·6	269·6	58 „ 760	0·107
Terchlor. of phosph. (PCl_3) .	51·4	244·4	78 ·5 „ 767	—
Chloride of zinc . . .	30·5	253·5	112 ·5 „ 752	—
Bisulphide of carbon . .	86·7	254·9	46 ·2 „ 769	—
Ether	90·5	268·2	34 ·9 „ 752	0·517
Iodide of ethyl . . .	46·9	254·7	71 ·3 „ 760	—
Oxalic ether . . .	72·7	291·4	184 ·4 „ 779	0·457
Acetic ether . . .	92·7	287·9	74 ·6 „ 762	0·474
Formic ether . . .	105·3	290·3	54 ·3 „ 762	0·485
Pyroxylic spirit . . .	263·7	303·5	65 ·8 „ 767	0·613
Iodide of methyl (C_4H_5I) .	46·1	252·8	42 ·2 „ 752	—
Acetate of oxide of methyl .	110·2	303·6	55 „ 762	—
Formiate of oxide of methyl.	117·1	282·8	32 ·9 „ 752	—

(1) Chem. Soc. Qu. J. I, 27.

Latent vapour-heat of different bodies.

A shows the latent heat of the weight-unit, B of equal volumes of the vapour (1 litre) at the boiling point.

Latent Vapour-Heat.—Person(1), on the assumption that the absolute zero was at -160^0 has constructed a formula analogous to that for latent fusion-heat (page 55), for the relation existing between latent vapour-heat, boiling point, and specific heat of bodies in the state of fluids and of vapours. He considers the latent vapour-heat to be the difference between the total amount of heat in a liquid, and that in the vapour at the boiling temperature. If the latter be termed T, the average difference of the specific heat of the liquid and vapour d, the latent vapour-heat was $= (160 + T)\,d$. He has calculated d for several substances, of which the boiling point T, the specific heat in the liquid state, and the latent vapour-heat are known. In this case, however, the values of L and d do not refer to weight-units, but to atomic weights, (the formulæ adopted corresponding to 2 volumes of vapour, O being $= 1$, $H = 0{\cdot}125$, $C = 0{\cdot}75$, &c.); the column Tot. Am. gives the total amount of heat contained at the boiling point in one atom of the vapour, [that is, $(160 + T)\,A.\,c + L$, A representing the atomic weight, and c the specific heat in the liquid state].

Substance.		L	Tot. Am.	d	Substance.	T	L	Tot. Am.	d
Ether	35°·7	126	898	2·17	Oil of turp.	156°·8	653	1764	2·06
Bisulphide of carbon	46 ·6	502	719	2·42	Sulphur .	316 ·0	724	1392	1·52
Pyroxylic spirit	66 ·5	582	866	2·56	Sulph. acid	326 ·0	718	1791	1·53
Alcohol . . .	78 ·8	597	1024	2·50	Mercury	350 ·0	775	988	1·52
Water	100 ·0	602	892	2·31					

He finds, that d varied but little and uniformly, and that the total amount of heat in several vapours, differing widely in their composition and temperature, was nearly the same.

Person had already asserted in 1843, that the latent vapour-heat was the same for substances of the same boiling points, and that, with other bodies, it varied with the boiling point. In support of this assertion, he subsequently brought forward(2) a series of substances of which the boiling points had been communicated to him by Favre and Silbermann. The formulæ and atomic weights have reference to the assumptions before-mentioned.

(1) Compt. Rend. XXIII, 337; Instit. 1846, 277; Pogg. Ann. LXX, 302,

(2) Compt. Rend. 524; Instit. 1846, 302; Pogg. Ann. LXX, 386; Ann. Ch. Pharm. LIV, 185.

Patent vapour-heat.

Substance.	Composition.	Boiling point.	Latent heat.	
			For the atomic weight.	For the unit of weight.
Ether	$C_4 H_5 O$	35°·6	421·3	91·1
Pyroxylic spirit . . .	$C H_2 O$	66 ·5	527·7	263·8
Acetic ether . . .	$C_4 H_4 O$	74 ·0	582·0	105·8
Alcohol	$C_2 H_3 O$	78 ·4	598·8	208·3
Butyrate of oxide of methyl .	$C_5 H_5 O_2$	93 ·0 ?	556·5	87·3
Water	HO	100	603·0	536·0
Formic acid	$C_2 H_2 O_4$	100 ·0	694·0	120·7
Oxide of amyl . . .	$C_{10} H_{11} O$	113 ·0	685·0	69·4
Acetic acid	$C_2 H_2 O_2$	120 ·0	382 0	101·9
Fusel-oil	$C_5 H_6 O$	132 ·0	606·8	121·1
Oil of turpentine . . .	$C_{20} H_{16}$	156 ·0	584·0	68·7
Terebene	$C_{20} H_{16}$	156 ·0	571·0	67·2
Oil of lemons . . .	$C_{20} H_{16}$	165 ·0	595·0	70 0
Butyric acid . . .	$C_4 H_4 O_2$	164 ·0	632·0	114·9
Valerianic acid . . .	$C_5 H_5 O_2$	175 ·0	660·0	103·5
Hydrocarbon . . .	$C_{12} H_{12}$	198 ·0	629·0	59·9
Hydrocarbon . . .	$C_{15} H_{15}$	255 ·0	783·0	59·7
Ethal-alcohol . . .	$C_{16} C_{17} O$	360 ·0 ?	881·0	58·4

As a general rule, the latent heat (for the atomic weight) increased with the rise of the boiling point; Person explains the exceptions in the following manner: With acetic acid, the results were influenced by the formula assumed, not being exactly equivalent to 2 volumes of vapour; (he recalls the inconstancy of the density of its vapour, as pointed out by Cahours and Bineau). The same would hold good for butyric acid, and perhaps also for butyrate of oxide of methyl (with the latter an assumption of this view would scarcely be justified; variation with the temperature of the relative vapour-densities having by no means been found in the case of ethers). The formic acid employed contained water. With oil of turpentine a concordant result was obtained, if the latent heat of the weight-unit were taken at 76·8, according to Despretz. In general the increase of the latent vapour-heats were parallel to the rise of the boiling points.

L. Smith(1) has called attention to the fact, that water may be frozen in vacuo even without the presence of absorbents of aqueous vapour, if contained in a vessel, the interior of which is lamp-blacked.

Spheroidal state.—Boutigny(2) gives the following definition of

(1) Sill. Am. J. [2] I, 265; Pogg. Ann. LXX, 171; Ann. Ch. Pharm. LXIV, 185.
(2) Compt. Rend. XXVI, 320; J. Chim. Méd. [3] V. 3.

Spheroidal state.

the phenomenon usually known under the name of Leidenfrost's experiment; a body placed upon a heated surface is in the spheroidal condition, when, assuming the globular form, and remaining on that surface out of the sphere of both physical and chemical action, it reflects the radiant heat, its molecules being with reference to heat in a stable equilibrium, *i. e.* its temperature being constant, or only changing within very narrow limits.

Faraday(1) succeeded in rapidly freezing mercury by a mixture of ether and condensed carbonic acid, after it had assumed the spheroidal state in a red-hot platinum crucible; certainly, a very remarkable phenomenon, the mercury freezing in a red-hot crucible.

Moritz(2) states, that even upon glass, water may be easily obtained in the spheroidal state, when placed at the boiling temperature upon a heated glass surface.

"Bumping" in boiling Liquids.—By the observation that liquids freed from air may be heated above their boiling points, without entering into ebullition, Donny(3) had been led to suppose that liquids possessed a much more powerful cohesion than is usually ascribed to them; that the formation of vapour took place only at the surface of the fluid, or when a bubble of air was contained in it; that the boiling point depended on the amount of air absorbed by the liquid; finally, that the so-called bumping of liquids during ebullition was due to the circumstance that the greater part of the air being expelled, the formation of a bubble of vapour could only take place at long intervals. Louyet(4) contests these views, and endeavours to account for the above phenomena by the increased attraction of the sides of the vessel for the fluids.

Redwood(5) recommends the use of glass vessels, coated inside with silver or platinum, for the distillation of substances liable to bump during ebullition.

Volatility of Fixed Substances with Steam.—It is known that some bodies—for instance, boracic acid—of a very fixed nature *per se*, when dissolved in a liquid, volatilize with the vapours of the solvent, when heated to ebullition. Larocque(6) has found this to be the case with a great number of substances.

(1) Ann. Ch. Phys. [3] XIX, 383; Pogg. Ann. LXX, 580; J. Pr. Chem. XL, 374.
(2) Pogg. Ann. LXXII, 112.
(3) Ann. de Phys. [3] XVI, 167; Pogg. Ann. LXVII, 562.
(4) Instit. 1848, 294.
(5) Pharm. Trans. VIII, 78.
(6) J. Pharm. [3] XIV, 345.

Relation between Composition and Boiling Point.—H. Kopp(1) has pointed out that the boiling points of analogous chlorine and bromine compounds differ 32°, 2 × 32 = 64°, or 3 × 32 = 96°, if respectively, 1, 2 or 3 atoms of chlorine in the one, are replaced by bromine in the other substance. Relation between composition and boiling point.

Tension of Vapours.—Babo(2) has compared the elasticity of the vapour of saline solutions with that of steam. At the temperature at which a saline solution boils, and the vapour formed balances the pressure of *one* atmosphere, steam possesses a higher elasticity. Babo has investigated the connection existing between the difference of these elasticities, and the amount of salt in solution; he found that for an increase in geometrical ratio of this difference the quantities of the salt added to 100 parts of water to form the solutions in question, likewise rose in geometrical proportion. (The boiling points of saline solutions of different degrees of concentration were taken from Legrand's observations, which several experiments had proved to be correct). We give, as an illustration, the following table, in which A represents the boiling point of a salt-solution at 760^{mm}, containing for 100 of water, the quantities of chloride of calcium indicated in column C, and B (in atmospheres of 760^{mm}) the elasticity of aqueous vapour at the given temperature.

A	B	C Observed.	Calculated.
102°·5	1·1	19·05	19·05
105 ·1	1·2	29·72	29·09 = 19·05 × 1.526
110 ·0	1·4	44·0	44·42 = 19·05 × $1·526^2$
117 ·7	1·8	66·7	67·84 = 19·05 × $1·526^3$
129 ·7	2·6	103·67	103·59 = 19·05 × $1·526^4$
146 ·5	4·2	157·95	158·19 = 19·05 × $1·526^5$

The quantity of a salt that produces, with 100 parts of water, a solution boiling at the temperature at which the elasticity of steam is $= 1 + (0·1 \times 2^n)$ atmospheres, may hence be expressed by $S \times F^n$. Babo has ascertained the values S and F for the following salts (all considered as anhydrous):

	S	F		S	F
Chloride of calcium . .	19·05	1·526	Nitrate of potassa . . .	34·30	2·31
Chloride of strontium .	28·65	1·55	„ soda	23·45	1·999
Carbonate of potassa . .	28	1·55	„ lime	33	1·58
Acetate of potassa . . .	24·30	1·73	„ ammonia . .	25·9	2·083

(1) Ann. Ch. Pharm. LXVII, 356; Pharm. Centr. 1849, 123.
(2) "Ueber die Spannkraft des Wasserdampfs in Salzlösungen," Freiburg, i. B. 1847.

Tension of vapours.

He finds a connection to exist between the values F, and the specific volume of the salts, inasmuch as the values $F^{1\cdot7}$, are nearly proportionate to the specific volumes.

Babo found that at temperatures below the boiling points, the elasticity of the vapour of chloride of calcium solutions, of varying concentration, diminishes in the same ratio; for instance, a solution of chloride of calcium, boiling at a temperature of 118°, at which temperature the elasticity of the vapour of pure water is = 1·8 atmospheres appears to give, at all temperatures, vapour of an elasticity 1·8 times smaller than that of pure water. The same simple relation does not exist with solutions of other salts. We add, expressed in millimetres, the following determinations by Babo, of the elasticity of aqueous vapour rising from chloride of calcium solutions at different temperatures: A (boiling point 118°), B (110°), C (105°).

	40°	45°	50°	55°	60°	65°	70°
A . .	28	38	49	62	79	100	123
B . .	38	50	65	81	103	127	159
C . .	—	58	76	97	125	150	188

Farey(1) communicates the following results, obtained in measuring the elasticity of steam by Southern, a mathematician employed in Watt's factory, in 1814.

Atmospheres.	Pressure in English inches of: Mercury.	Temperature° C.
1	29·8	100
2	59·6	121·25
4	119·2	145·2
8	238·4	173·1

Alexander(2) gives a formula of interpolation for the elasticity of steam:

$$p = \left(\frac{t}{180} + \frac{990}{1695}\right)^6$$

in which p represents the elasticity in English inches, t the temperature according to Fahrenheit, 180 the known fundamental space of this thermometer-scale, 990° the latent vapour-heat, 1695 the increase of volume on the conversion of water into steam.—This formula is tolerably applicable to high, as well as low temperatures; the theoretical deduction is, however, unintelligible, and of no value.

(1) Phil. Mag. [3] XXX, 113.
(2) Sill. Am. J. [2] VI, 210; Phil. Mag. [3] XXXIV, 1 and 98.

The form of the expression is by no means new, corresponding, as it does, with the formulæ of Young(1), Coriolis(2), Tredgold(3), Mellet(4), Spasky(5), and Dulong(6).—Alexander has, for comparison with his formula, arranged synoptically the measurements made by Watt (1774), Robison (1778), Betancourt (1790), Southern (1797—1803), Dalton (1801 and 1820), Ure (1818), Arzberger (1819), Taylor (1822), the French Academicians (1829), the Franklin Institute (1836), and by Regnault (1844). Tension of vapours.

Shortrede(7) has given a review of the different formulæ proposed for the expansion of aqueous vapour. He himself has constructed a formula precisely similar to that of Magnus, for the temperatures of the mercury-thermometer, and for the atmospheric pressure of 0·76^{m} as unit, namely $\log A = 5 - \frac{1625}{225 + t}$ for the centigrade scale, or $\log A = 6{\cdot}47712125 - \frac{2925}{373 + t}$ for the Fahrenheit scale, and for the elasticity in English inches of mercury.

Faraday, finding that a gold leaf suspended over mercury below 0^{0} exhibited no change, had concluded from this experiment that vapour was no longer evolved from mercury at this temperature. G. Karsten(8) has observed that the sun-picture on a daguerreotype plate will become visible on exposure over mercury even below 0^{0}, proving that this metal vapourizes even at that temperature.

Formation of Dew.—Melloni(9), incited by an opposition which, long ago given up in other places, seems still to be maintained here and there in Italy, against Wells's theory of the formation of dew, has subjected this theory to revision, and has not only confirmed it in all essential points, but has also enriched it with some accurate determinations and observations of his own.—His apparatus consisted of three concordant thermometers, whose bulbs were surrounded with thimble-like, polished, silver vessels, while cylinders of tinned plate enclosed their graduated spindles. The metallic cover of one thermometer was blackened, those of both the others were bright; the instruments were inserted in a horizontal position, through lateral apertures,

(1) Pogg. Ann. XXVII, 21.
(2) Gehler's Phys. Woerterb. X, 1065.
(3) Pogg. Ann. XXVII, 22.
(4) Ibid.
(5) Pogg. Ann. XXX, 333.
(6) Idem. XVIII, 137; XXVII, 23.
(7) Instit. 1848, 220.
(8) Pogg. Ann. LXXI, 245.
(9) Ann. Ch. Phys. [3] XXI, 145; XXII, 129, 467. Compt. Rend. XXIV, 530, 641; XXV, 499. Pogg. Ann. LXXI, 416; LXXIII, 467.

Formation of dew. into three boxes of tinned plate, widening conically upwards, and resting on thin metal feet. So long as the three boxes were closed above with covers, the thermometers showed the same temperatures; when, however, the covers were removed from the blackened thermometer, and from one of those with the metallic surface, the temperature of the latter fell 0°·108, while that of the blackened one fell 3°·581; a plain proof that radiation, not the contact of the outer air, is the cause of the difference of temperature.

Melloni found that the radiation was strongest towards a circular space of 30° or 35° apparent radius, reckoned from the zenith, while the discrepancies of the thermometers diminished and disappeared as the axes of the metal boxes approached the horizontal position, or when clouds spread over and veiled that part of the sky.

The deposition of dew was always preceded by a cooling, and the slight radiation of metals, entirely explains why they do not become bedewed. The following experiment irrefragably demonstrates this. A disc of tinned plate was varnished on one side at its central part, and at some distance above it, on the same axis, was fixed a bright metallic plate, which, however, left uncovered a ring of the varnished part; the whole was then exposed vertically in a clear still night. The dew, which appeared immediately on the free varnished surface, spread itself towards the metallic margin, more than towards the blackened central part, which could become cooled only by conduction. Exactly the same phenomena were repeated on the lower bright side of the metal disc that was turned towards the ground; here also the central part remained dry. The upper plate of metal, which was brightly polished, was not at all bedewed. This simple experiment illustrates all the points discussed by physicists concerning the origin of dew, inasmuch as it shows that the dew neither falls from above, nor rises from below, and that the metals exert no peculiar repulsive power upon water-vapour(1).

Melloni remarks, that he never found greater differences than 1° or 2° between the temperature of the radiating body and that of the surrounding air, and that Wilson and Wells had observed differences of 7° or 8°, only because they placed the thermometers at

(1) Zantedeschi, however, disputes the result of the experiment here adduced, and asserts that he has always found the upper disc, as well as the varnished surface, bedewed, if the dew on the night of the experiment has risen at all to the height of the discs. Zantedeschi maintains, that the dew originates in water-vapours exhaled from the ground. (Arch. Ph. Nat. VII, 59. Delle alterazioni fatte dal Sign. Melloni alle dottrine sulla rugiada e sulla brina dei Sign. Fusiniere e Zantedeschi; L'ipotesi di Wells; in Raccolta Fisico-Chimica Italiana, III).

Formation of dew.

very unequal distances from the ground. A special explanation is indeed requisite for this, that so slight a difference as one of 2° can induce a condensation of water-vapour, and a copious deposition of dew; and it is necessary to conceive the theory under a somewhat altered view. Melloni remarks, in the first place, that this difference of temperature between the radiating bodies and the surrounding air, is independent of the temperature of the latter, and he adduces, in confirmation of this, the observations of Parry and Scoresby, as well as of Pouillet. His own observations with thermometers, of which the bulbs were wrapped with cotton-wool and wool, in various degrees of compactness, gave the most marked fall of temperature when the envelopes were most loose. Here the strata of air, which remain between the fibres and become cooled, promote a farther cooling of the thermometer: But the same holds good for the air, which is retained near the surface of the earth among thick vegetation, and, therefore, the difference of temperature (between the radiating plants and the surrounding air) necessary to induce the state of saturation with aqueous vapour, is by no means so great as has been hitherto assumed in all text-books of physics. It explains why the deposition of dew is so copious and universally diffused when it once appears at all. Melloni distinguishes three horizontal strata in the air which surrounds the plants. The highest stratum is in contact with those parts of the plants that are radiating most strongly. This air falls down and becomes still farther cooled in the middle region, where the vegetation is thicker, and still subject to radiation; it is here that the dew-point occurs. The air now falling down quite to the ground, and between the lower parts of the plants, which are entirely protected by the upper, becomes warm again, and rises loaded with the moisture of the soil, again to commence the same route. This circulation is the special condition of the formation of dew. Hence it is intelligible why a draught of air opposes its deposition; why, in very dry air, dew is met with only near moist ground and stagnant water, and why the higher trees, exposed as they are to air-currents, and surrounded with a drier atmosphere, are so little liable to be bedewed. Melloni farther deduces, from his principles, why dew does not occur on the little Polynesian islands, and on ships on the high seas, and why, on the contrary, it appears copiously, as soon as the ships approach the coasts of continents: he explains the sharp night-chills in the deserts of Africa, as well as the freezing of shallow water under an atmospheric temperature of 5° or 6°, while water has been proved to be unable, by simple radiation, to cool itself quite 2° below the temperature of the air.

Influence of colour on the formation of dew.

Influence of Colour on the formation of Dew.—Brocklesby(1) has instituted experiments on the dependence of dew-formation, and consequently of radiating power, on colour, by exposing variously coloured pieces of flannel of exactly similar texture, and pieces of glass and of pasteboard, coated with different colours, to nocturnal radiation. The experiments of Melloni, which have settled this question, as well as those of Knoblauch, are not mentioned by Brocklesby. His experiments, however, likewise prove that colour has, of itself, no influence on these phenomena.

Atmidoscope.—Babinet(2) has constructed an *Atmidoscope,* which shows the rate of evaporation taking place, in a given locality, according to the degree of dryness of the air, and its temperature and motion. A reservoir of porous plastic clay is filled with water, and the consumption is measured by a tube, which is in connection with it. Babinet holds, that his instrument has these advantages over the ordinary hygrometer, that it is affected by the movements of the air, and that it indicates the whole amount of action from the moment, at which it is set, to that of observation.

An hygrometer has been described by Majocchi(3), and an improved construction of the same by Regnault(4).

Heat-conduction in the Ground.—Dove(5) has found, by means of observations of the temperature of the ground at Brussels, at Heidelberg, and at Schwetzingen (the first made in stiff clay, the latter in light sandy soil), and farther by observations which have been made at Edinburgh since 1837, in dolerite, coal-sandstone, and sandy soil, at depths of 3, 6, 12, and 24 Parisian feet, that the amount of the periodic, as well as of the non-periodic variations of temperature are slightest in dolerite, more considerable in sand, and strongest in sandstone.

Heat-conduction in Crystals.—As, according to Mitscherlich, the expansion by heat, according to Savart, the elasticity, and, according to the known laws of double refraction, the dispersion of light, are dependent on the position of the crystalline axes, so this is also the case, according to Senarmont's(6) experiments, with the conduction of heat. Senarmont passed through the middle of, and perpen-

(1) Sill. Am. J. [2] VI, 178.
(2) Compt. Rend. XXVII, 529; Instit. 1848, 158.
(3) Ann. Ch. Phys. [3] XIX, 77.
(4) Ibid. 82; Pogg. Ann. LXX, 530.
(5) Berl. Acad. Ber. 1847, 32.
(6) Compt. Rend. XXV, 459, 707, 829; Ann. Ch. Phys. [3] XXI, 457; XXII, 179; Pogg. Ann. LXXIII, 191; LXXIV, 190; LXXV, 50; Sill. Am. J. [2] V, 114.

Heat-conduction in crystals.

dicularly to, the plates of the crystal which he used, a platinum wire, heated by the voltaic current, or, instead of this, a fine metal tube, which, when heated on one side over a lamp, was traversed by a current of hot air, or lastly, he placed the plates on the fine point of a heated silver wire. The plates had, at most, a diameter of 38 millimetres, and the diffusion of the heat on them was graphically represented according to the method of Ingenhouss, the plates being coated with pure wax, or with a mixture of wax and olive oil. When this coating melts, it recedes on the plate, as if it no longer wetted it, and forms a little wall, so sharply defining the isothermal line of the fusing-temperature of the wax, that, after cooling, the length of the major and minor diameters of its curve can be measured, as well as their inclination to any other direction conveniently assumed on the plane of the plate.

By slitting plates from the same crystal in various directions, it was thus possible to ascertain the form of the isothermal surfaces. The chief result of Senarmont's research was, that these isothermals, in the case of crystals having two optic axes, are either ellipsoids with three unequal axes, or, at least, surfaces, which approach very nearly to such ellipsoids. In all crystals optically uniaxial they pass into ellipsoids of revolution, whose axis coincides with the optic axis; in homogeneous amorphous bodies, as well as in crystals of the regular system, the isothermal surfaces are spheres. —Generally, the principal thermal axes coincide with the optic axes of elasticity, and exceptions occur only where,—as in the oblique prismatic (monoclinometric) system for those axes, which lie perpendicularly to the axis of symmetry; and in the doubly-oblique prismatic (triclinometric) system, for all three axes,—even the colour of the light implies a difference in their position, so that we may always imagine a wave-length, whose proper axes of elasticity actually coincide with these thermal axes.

The bodies examined by Senarmont were—

I. Homogeneous plates of plate-glass and of zinc; three plates of fluor-spar, parallel respectively to a surface of a cube, of an octohedron, and of a rhombic dodecahedron; plates of iron pyrites, magnetic iron ore, red oxide of copper, galena, and blende.

II. From the square prismatic (tetragonal, pyramidal) system:—of cassiterite (binoxide of tin), rutile, idocrase, and subchloride of mercury, plates cut perpendicularly, as well as parallel, to the axes. The first gave circles, the latter ellipses, the proportions of whose axes were, for rutile = 1·27, for idocrase = 1·13, for subchloride of mercury = 1·23.

Heat-conduction in crystals.

III. From the right prismatic (hexagonal, rhombohedral) system:—calcareous spar, quartz, beryl, specular iron ore, and corundum. The result was as in the preceding system; the proportions of the axes of the ellipses being, for calc-spar = 1·12, for quartz = 1·312, for beryl = 1·11. The thermic properties fail of perfect coincidence with the optic, inasmuch as, both in quartz, in subchloride of mercury, and in rutile (that is, in so-called optically attractive crystals) and also in calc-spar and beryl (that is, in repulsive crystals), the thermic ellipsoid is a prolate one. However, the oblate ellipsoids have hitherto been found only in the case of the repulsive (idocrase, specular iron ore, and corundum), the most prolate in attractive crystals. To explain these phenomena we must assume the heat as corresponding to light-rays, which lie beyond the extreme red.

IV. From the rhombohedral system:—heavy-spar and topaz, which gave no decided results; also arragonite, bournonite, stibine, staurolite, and pinite, in which the three thermic axes lie parallel to the crystalline axes. The proportions of the axes of the ellipses were, in an arragonite-plate, parallel to the base of a rhomboidal prism, = 1·22; for bournonite, in a plate perpendicular to the base, and parallel to the greater diagonal = 1·31, and in a plate perpendicular to the base, but parallel with the lesser diagonal, = 1·29.

V. From the oblique prismatic (monoclinometric) system:—felspar, augite, wolfram, gypsum, glauberite, and adularia. Of the four first crystals, three plates were examined in every case; No. 1 vertical to the axis of symmetry, which in each is also a thermal axis: Nos. 2 and 3 parallel with the axis of symmetry, and with one of the other two thermal axes. The proportions of the axes of the ellipses are:

	Feldspar.	Augite.	Wolfram.	Gypsı
No. 1.	1·23	1·24	1·09	„
„ 2.	1·02	1·28	1·13	1·24
„ 3.	1·27	1·10	1·23	1·50

VI. From the doubly-oblique prismatic (triclinometric) system:—bichromate of potassa. The experiments with this substance gave no decided results.

The analogy between the thermic and optic properties was confirmed also by Senarmont's(1) experiments with substances, whose homogeneous molecular state was altered by their being compressed,

(1) Instit. 1848, 142; Compt. Rend. XXVII, 501; Ann. Ch. Phys. [3] XXIII, 257; Pogg. Ann. LXXVI, 119.

drawn, or tempered. Square plates, of 25^{mm} side-length, and of $6-8^{mm}$ thickness, compressed between the two parallel jaws of a vice, showed clearly thermal ellipses, whose lesser axes always fell in the direction of the pressure; that is, of greatest density. Experiments with porcelain, with plate-glass, and with flint-glass, gave axis-proportions from 1·031 to 1·098. In the case of bodies in which such a molecular state is artificially induced, a prolate or oblate thermal ellipsoid always corresponds to a similar form of optical surface of elasticity, but these bodies are also optically attractive or repulsive for all coloured rays without distinction, while there are crystals, as, for instance, apophyllite, which are attractive for one part, repulsive for another, and simply refractive for one middle part of the spectrum. **Heat-conduction in crystals.**

Bonnet(1) and Duhamel(2) have treated mathematically the problem of heat-conduction in bodies, whose conductivity is different in different parts and directions. The latter arrives at this conclusion among others, that according to whatever law heat may be supplied to all the points of a line which stands perpendicular to a thin plate of crystal, the isothermal curves are ellipses, whose axes lie parallel with two principal axes of the heat-conduction, and are proportional to the square roots of the corresponding values of the conductivity.

Bertrand(3) communicates the results of an essay on the simplification of calculations, relative to the motion of heat, by altering the coordinates.

Radiation of Heat.—By an extensive series of researches Knoblauch(4) has, in part, newly confirmed, and in part amplified, several most essential points of our knowledge of radiant heat; and, lastly, he has completely carried out the analogy between the behaviours of radiant heat and light. He made use of a multiplier, provided, when necessary, with thermo-piles of 15, 25, or 40 elements, which, for experiments on inflection and double refraction, were narrowed towards one side to a small vertical edge.—Concerning the *penetration of heat-rays* through diathermanous bodies, especially as depending on the temperature of the source of heat, it was previously known, that certain of these bodies permitted the passage of the heat in inap-

(1) Compt. Rend. XXVII, 49.
(2) Ibid. XXV, 870; XXVII, 129; Instit. 1848, 246.
(3) Ibid. XXVII, 557.
(4) Berl. Acad. Ber. 1846, 355; Instit. 1846, 21; 1847, 277; De Calore Radiante disquis. Berol, 1846; Pogg. Ann. LXX, 205, 337; LXXI, 1; LXXIV, 9, 161, 170, 177; Jahresber, üb. d. Fortschr. d. Phys. i. J. 1846, Berl. 280, 311.

Radiation of heat.

preciable times; that, for any given substance, the smoother its surface, the greater the amount of transmitted heat; that the loss, which the heat suffers by transradiation, becomes smaller in proportion as the thickness of the substance already passed through increases; that the radiant heat permeates various bodies in different proportions, and that these proportions have no relation to the transparency of the bodies; that the rays emanating from the same heat-source, which pass through various diathermanous substances in succession, suffer losses thereby, which vary according to the nature of these bodies, being, however, always greater than those which they sustain, by passing through a series of uniform materials; that heat-rays from different sources, which induce exactly equal elevations of temperature, penetrate the same substances in dissimilar proportions.—The experiments of De la Roche and of Melloni seemed to prove that the transradiant power of heat increases with the temperature of its source; only two observations indicating an exception, viz., that the heat-rays from all sources pass through pure rock-salt in the same proportion, and through lamp-blacked rock-salt in the greater degree, the lower the temperature of the source.—It appears from the experiments of Knoblauch, in which he employed, as heat-sources, red-hot platinum without flame, an alcohol-flame without a carbonizing wick, an Argand lamp, with a constant oil-level, with a cylindrical wick, and without a glass chimney; and, lastly, a hydrogen-flame, supplied from a gasholder under constant pressure, that the heats of the hydrogen-flame, and of the ignited platinum, notwithstanding the great difference of their temperatures, were equally capable of passing through a glass-plate, while that of the alcohol-flame possessed this property in a lower, and that of the Argand lamp in a higher degree. The heats of the flames of alcohol and of hydrogen pass equally through alum, and that of red-hot platinum even more freely; while the heat of the hydrogen-flame passes less readily, than those of the three other sources, through potassa-mica, and through magnesia-mica.—The rays from a Leslie's cube, gradually cooling, exhibited a power of penetrating through the most various substances, which was the same, whatever might be the temperature, between 30^0 and 100^0, of the origin of heat.—The rays, which proceeded from a cylinder of sheet iron, heated over an Argand lamp, passed, through some substances, better at a high than at a lower temperature; through others, equally well.—Of the rays, which are emitted from a platinum spiral heated, at first, lightlessly, then to redness, yellowness, and, finally, to whiteness, those from the red-hot and from the yellow-hot metal pass through

glass in the same proportion. Those of the yellow-hot pass less freely through alum, than those of the red-hot and of the dark-hot platinum, while their penetrating power for glass increases with the temperature. On these experiments collectively is grounded the conclusion, " *that the penetrating power of radiant heat, through diathermanous bodies, stands in* NO *direct relation with the temperature of its source.*" Radiation of heat.

With respect to the heating of bodies by radiation, it was known before: Firstly, that different substances were heated in different degrees, by the influence of one and the same source; Secondly, that the degree of heating of each substance is dependent on the quality of its surface; Thirdly, that one and the same body is equally strongly heated, by rays from different sources, which exert an exactly equal influence on a lampblacked thermoscope. Knoblauch proved,—by experiments with a metallic disc, which, on the side towards the thermo-electric pile, was coated with lampblack, and on the other side at one time with carmine, at another with black paper,—that the heating, for similar intensities of irradiation, is independent of the temperature of the source, and is determined alone by the nature of the absorbing substances, which are more receptive of certain rays than of others.

To ascertain the relation of the heating of bodies to their thickness, Knoblauch coated thin discs of metal plate, similar in every respect, with different thicknesses of—Firstly, transparent varnish; Secondly, of black, opaque, but diathermanous lac; Thirdly, of white lead; and exposed them to the radiations of the same heat-sources. The bodies *became heated,* within the limits of the experiments (100°, and the temperature of the Argand lamp), *the more highly, the greater their thickness.* That the experience of Leslie and of Melloni should have been the reverse arose from this, that they employed screens so thick, that only a small portion of the absorbed heat reached the sides which were turned to the thermoscope. There is, then, a limit, beyond which the heating of a body ceases to increase with its thickness, and which, for a given substance, depends on the nature of the origin of heat.—However, diathermanous bodies are most warmed by the rays, which are least able to pass through them.

Various substances radiate heat at the same temperature in different degrees. For a given substance this property is dependent, as well on the quality of its surface, as on its thickness. Knoblauch employed, as side-surfaces of Leslie's cube, leaden plates, some cast, some rolled, first polished, then simply, and last, doubly scratched, and found, as previously did Melloni, that an

Radiation of heat. alteration of the surface by scratching, &c., only influences its radiating power, so far as its density and hardness are changed. That power is increased or diminished, according as the substance is made looser or more compact in texture by the scratching.—Farther, by the employment of various thicknesses of varnish, he confirmed the result obtained by Rumford and by Melloni, viz.: that the radiating power increases with the thickness of the radiating surface. By comparison of this result with that quoted above, we arrive at a new proof of the conformity between the radiation and absorption of heat.—Their parallelism is absolute for the same bodies, so that all influences, which exalt or depress their radiation, exert the same action on their absorption; but in a comparison of different bodies we can by no means assert that one of them, which, at a given temperature, shows a higher radiating power, will, therefore, generally have a higher tendency to absorb heat, since the proportion, in which heat is absorbed by two bodies, varies with the nature of the rays. A plate of carbon, and a disc of metal-gauze coated with carmine, being exposed, first to the radiation of an Argand lamp, then to a dark source of heat at 100°, the first plate gave, with both sources, an equal, the carmine disc a greater deflection of the needle, under the influence of the dark rays. This distinction persisted *in the same degree*, when the second side of the carmine disc was lamp-blacked, and, therefore, plainly arises from a power of absorption, that is different for different sources of heat. Black paper behaves similarly, and these bodies have, therefore, with an unequal tendency to absorb, an equally great radiating power. The radiation of heat is the same, from whatever source the rays, which have warmed the radiating substance up to a given temperature, may proceed.

One of the best methods of determining the similarity or dissimilarity of heat rays, consists in examining whether they penetrate diathermanous substances in the same or in different proportions. Knoblauch employed this means for the decision of the question, whether the heat, which radiates from certain bodies at one and the same temperature, or within fixed limits of temperature, appears as heterogeneous, according as it is given off from one or the other body, or is supplied to them in dissimilar modes. Various diathermanous substances laid over the side-surfaces of a Leslie's cube, and heated between the temperatures of 30°—112°, also metal, wood, porcelain, leather, cloth, and pasteboard, heated by radiation from various sources, themselves gave off by radiation heats of exactly similar nature, *i. e.*, such as pass through diathermanous proof-plates in the same proportions.—However, the heat-rays, which come off

Radiation of heat.

from diathermanous plates heated by rays from an Argand lamp, behave differently in this respect. The heat proceeding from these plates consists of two parts, viz. of the appropriated specific heat, and of the heat radiated through them; the latter part is that, which determines their heat-colour, and therefore the differences of their behaviour towards other diathermanous plates. If a metallic cylinder, heated to 112⁰, or the heat developed by the vital process, as that of the hand, served as the source, diathermanous bodies, as well as adiathermanous, conferred perfectly similar penetrating power on the rays which they threw off.—The heat, therefore, which escapes from different bodies, between the temperatures of 30⁰ and 112⁰ under the most dissimilar circumstances, is recognised as perfectly similar.—The method adduced gives, at the same time, a ready means of examining, whether a body transmits heat or not. It is heated by means of an Argand lamp, and the penetrating power of its heat-rays is examined by a series of diathermanous plates. If results are obtained the same as from a body established as adiathermanous, then the substance under examination also belongs to this class. Differences can only arise from the passage of chromatic heat. Thus, black glass, black asphalt-varnish, a thin layer of carmine, letter-paper and ivory proved to be diathermanous.

The dispersion of heat, or its diffusion by reflection, was first proved with certainty, and closely investigated by Melloni. He found that the diffusion from a white surface has a different intensity for different heat-rays. The metals only diffuse the heat of all sources with equal strength; lampblack (carbon) exhibits scarcely any perceptible diffusion.—The intensity of the diffused, is like that of the regularly reflected, heat, dependent on the nature of the substance, and on the quality of its surface; one essential distinction between this diffusion and regular *(spiegelnden)* reflection, consists in this, that, in the first case, the heat-rays of different sources are thrown back from the same substance in different proportions, and that the heat-colour of the diffused rays is generally different from those of the directly reflected, or of the incident heat, as follows unquestionably from Knoblauch's experiments.—The diathermanous proof-plates served again to establish this proposition; *i. e.* it was ascertained whether the radiant heat penetrated the same diathermanous media in various proportions, accordingly as it was employed in the state of direct or of diffuse reflection from various bodies.—In these experiments the heating of the dispersing substances was avoided, by covering with them the sides of a metal-cube, which contained water of the temperature of the surrounding medium. To obtain the

Radiation of heat. action of a direct radiation, similar under all conditions, and therefore results comparable with each other, the distance, inclination, and magnitude of the dispersing surface had to be altered in a great variety of ways. Decisive experiments proved, that the passage of diffused heat, through diathermanous plates, was not affected by these changes. The heat radiated from various colouring matters, from bodies of similar nature, but differently coloured, and lastly from dissimilar bodies of the same colours, clearly showed well marked differences as regards its passage through the proof-plates. The annexed table, for instance, shows the behaviour of the rays of an Argand lamp, according as they were dispersed by a series of coloured, white, or black surfaces.

Many bodies of similar nature change the heat in an exactly similar manner, such as, for instance, birch-wood, cork, and mahogany, as also the metals and metallic alloys, which, besides, give back the diffused heat exactly as it falls on them,—a result agreeing with the proposition of Melloni, that rough metallic surfaces behave towards heat, just as do white surfaces towards light.—The chief result is, that there are many bodies, by dispersion from which the heat-colour is very much altered, while from others it is not at all; and that this alteration is independent of the roughness of the surfaces; the metals retain their whiteness of heat-colour, whether they are employed rough or burnished.—Numerous instances prove that the change, after diffusion, of the power possessed by heat of passing through one diathermanous substance, stands in no sort of relation to its transmission through any other.

From the examination of the influence of the sources of the heat on its diffusion, it appeared, that the alteration of the heat-colours, which is very considerable in the case of an Argand lamp, is less in that of red-hot platinum, yet smaller for the rays of an alcohol-flame; and, for those of an iron cylinder of any temperature between 24° and 112°, it is absolutely nothing. Generally, therefore, the changes which heat undergoes by diffused reflection, are dependent as well on the nature of its origin, as on the quality of the reflecting substances.—Knoblauch found, by repeating the experiments with the four above-mentioned sources of heat, that the surfaces, which exert an *equal influence* on the rays of one of them, for instance, of the Argand lamp, also modify the rays of the other sources in the same manner.

Two explanations of the change which the heat-rays suffer under diffused reflection, suggest themselves. It rests either on an actual alteration of the heat-rays, or only on an elective absorption on the

Radiation of heat.

part of the dispersing surfaces. If the latter be the case, a variation of intensity of the heat-rays must accompany their difference in penetrating power. Thus, for example, the heat diffused by white paper has a greater power than that reflected from black paper, of passing through red glass and through calcareous-spar. Again, the heat of Argand lamps contains more rays of the heat-colour of red glass and of calc-spar, than do those of an invisibly-heated cylinder. Accordingly, if a partial absorption is the cause of the heat-colours of the diffused rays, white paper must be proportionally a worse reflector of the heat of the latter source, than of that of Argand lamps, if the diffusion of both sorts of rays by black paper is chosen as the standard of comparison. Experiment establishes this, and it follows from an extensive series of similar observations:—Firstly, That a surface, which reflects heat, so that it shall pass, in a higher degree than that thrown back from another surface, through red glass, blue glass, alum, rock-salt, calcareous-spar, and gypsum, will reflect in comparison with this second surface, most highly the heat of Argand lamps, next that of red-hot platinum; in a lower degree, that of alcohol-flames; and in the lowest, that of the heated cylinder: this, too, at the same time, implies the converse, that a reflecting surface, which, in comparison with another, diminishes the penetration of heat through the substances here mentioned, reflects the rays of Argand lamps, proportionally, in the lowest degree; those of red-hot platinum in a higher; with yet greater intensity the rays of alcohol flames; and, relatively, with the greatest, those of the lightless cylinder:—Secondly, That, if the heat-colours of certain proof-plates are ascertained to be more homogeneous with one dispersing surface, and of other plates more with a second surface, the first surface also reflects the rays of various heat-sources in some cases more strongly, in others more weakly, than does the second:—Thirdly, That, on the contrary, if the reflected rays behave similarly towards diathermanous plates, both surfaces also throw back the rays of different heat-sources with equal intensity.—The collective result is, therefore, that the alterations of the heat by diffused reflection are only the consequences of an elective absorption, exercised by the reflecting surfaces, over certain of the rays thrown upon them.—The phenomena are analogous to those, which have been observed in the diffusion of light, while, as Herschel and Melloni had already remarked, the analogy of the two sorts of rays does not extend to their reflection.

The researches of Knoblauch teach us, with reference to the heat sources, which he employed, that the variety of the rays emitted

Radiation of heat.

is greatest from the Argand lamp, less from the red-hot platinum, and yet less from the alcohol-flame, while it disappears altogether in the case of the cylinder heated to 100°; in fact, the heat radiated from the most different solid bodies, between 30° and 112°, is entirely *homogeneous*, or *monochromatic*.—Knoblauch, by making use of a platinum spiral, which was heated over the chimney of a Berzelius lamp, from below 112°, through redness and yellowness up to whiteness, found, by testing it with diathermanous plates, that the variety of the heat-rays emitted from the same body increases with the temperature.

De la Provostaye and Desains(1) have instituted some researches on the radiation of heat, which are to be regarded as a continuation of an earlier essay(2).

Dulong and Petit, during their researches on cooling in air-filled space, had thought that the action of air under a pressure p might be represented by $n.\ p^{0.45}$. De la Provostaye and Desains show, that the mode by which this expression was arrived at, does not exclude a formula $n.\ p^{0.45} + f(p)$, if f(p) vanishes with p, and is constant within the limits of their experiments. The experiments on cooling *in atmospheric air* have proved that at a low pressure there is a point of flexure in the curve, which represents the dependence of the rate of cooling on the pressure. In hydrogen De la Provostaye and Desains obtained the following results:

Pressure . . .	$0^{m}.760$	$0^{m}.477$	$0^{m}.057$	$0^{m}.020$	$0^{m}.0044$
Time of cooling	12′46″	13′20″	13′40″	14′49″	27′24″

The cooling, therefore, proceeds the more slowly as the rarity of the gas increases. In the case of *carbonic acid*, the time of cooling increases with the diminution of the pressure up to 35^{mm}, remains then equal up to 12^{mm}, and then diminishes. *Protoxide of nitrogen* behaves in an exactly similar manner.—The cooling in a mixture of equal volumes of hydrogen and atmospheric air, under a total pressure of 60^{mm} proceeds more slowly than in hydrogen under 30^{mm}; so that here, therefore, the action of the air is retarding, while alone it would act as accelerating. The molecules of gases seem to act on each other, so as to diminish their mobility.—In reference to the intensity of radiation, De la Provostaye and Desains have substituted, for the known formula of Dulong and Petit, a more comprehensive expression, and have proved its accordance with the results of observation. If the temperature of the thermo-

(1) Ann. Ch. Phys. [3] XXII, 358; Compt. Rend. XXIV, 60, 684, 967; XXV, 106; Arch. Ph. Nat. IV, 174.
(2) Ann. Ch. Phys. [3] XVI, 384.

electric pile in two experiments is t and t′, and T and T′, that of the source of heat—the ratio of the deflections of the needle is expressed, Radiation of heat.

$$R = \frac{a^{\vartheta + \alpha\vartheta^2 + \beta\vartheta^3} - 1}{a^{\vartheta_1 + \alpha\vartheta_1 + \beta\vartheta_1^3} - 1}$$

where $a = 1{\cdot}009$, $\vartheta = T - t$, $\vartheta_1 = T' - t'$, $\alpha = \frac{1}{7028}$, $\beta = \frac{\alpha}{100}$

The same physicists compared the radiating power of metals, in two different methods, with that of lampblack as unity, and obtained the following results :

Metals.	Radiating power.	
	1st. Method.	2nd. Method.
Silver, solid, rolled	0·03	0·029
Do. chemically precipitated on copper (dull surface)	0·0536	0·053
Do. Do. Do. and polished . .	0·0225	0·022
Do. silvered	—	0·0205
Do. solid, polished	0·025	0·022
Do. Do. after long heating	0·0275	0·0297
Do. plated on metal	—	0·104
Platinum rolled	0.108	0·104
Do. polished	0·095	0·09
Gold-leaf	0·0128	0·043
Sheet copper	0·049	0·0514

These values are considerably less than those which the experiments of Leslie and of Dulong and Petit assign to the radiating power of the metals.—Knoblauch(1) seeks to account for these discrepancies, by the variability of the radiating power of lampblack, as proved by Melloni; and he points out that this magnitude is no longer admissible as a standard. However, only thus much seems to follow from Melloni's research, that the layer of lampblack must be made sufficiently thick, to obtain a constant maximum of radiation, and it does not appear from the treatise of the French physicists, that they have neglected this precaution.

The first of the two above-mentioned methods of determining the radiating power, consists in exposing [illegible] thermo-electric pile to the influence of the hot surfaces, of which, [illegible] the case of the metals a larger, and of the lampblack a smaller extent was admitted to action, by means of a perforated screen.—In the second method two

(1) Jahresber. der Berliner Phys. Gesellschaft fur 1846, 279.

Radiation of heat.

equal surfaces were employed, the metallic ones, however, at a higher temperature, and, from the deflection which the lampblack surface gave at T, that which would occur at the higher temperature T′ of the metal was calculated by the formula

$$\delta' = \delta \cdot \frac{a^{T' - \vartheta} - 1}{a^{T - \vartheta} - 1}$$

so that the magnitudes obtained were comparable. We here insert the corresponding results obtained by some other physicists. Melloni, incidentally to some researches on the formation of dew, has measured the radiating power of some substances, with which he coated the metallic cases of his thermometers. He found, taking the power of lampblack at 100, for

Silver	3·026	Herbs with smooth leaves	103
White-lead	99	Leaves of elm and poplar	101
Varnish	97	Sawdust of poplar	99
Isinglass	96	" mahogany	95
Glass	93	Gravel	93
Graphite	86	Vegetal mould	92

A thermometer, whose bulb was covered with one coat of varnish, cooled six times less than another with eight coats of varnish;—a proof that the radiation proceeds from points beneath as well as on the surface.

Masson and Courtépée(1) have instituted experiments on the radiating power of many substances in the form of extremely fine precipitates; they thence concluded—Firstly, That the metals, in the state of fine division, have a considerably greater power of radiation than when they are cast or hammered; Secondly, That this power of bodies depends on their state of cohesion, but not on their general nature; Thirdly, That all bodies, if reduced to the same state of fine division, would have, at 100° the same radiating power. In a subsequent communication(2) they add, that bodies in a state of extreme comminution seem, even at 400°, all to have equal powers of absorption and of dispersion, that all substances which entirely absorb light, exert also an equal action on the heat-rays; that all substances, not black, exhibit the same power of absorption and diffusion, and this also for luminous rays, through whatever sub-

(1) Compt. Rend. XXV, 936; Sill. Am. J. [2] VI, 355.
(2) Compt. Rend. XXVII, 592; Instit. 1848, 358.

stances they may have passed. Phosphate of lime alone is stated to have a diffusing power very weak in proportion to its strength of absorption. Radiation of heat.

Glaisher has communicated to the Royal Society of London(1) some results concerning the nocturnal radiation of heat, which he obtained with nearly 100 different substances.

De la Provostaye and Desains have also measured the reflecting power of metals, by causing the rays of a Lokatelli's lamp to be reflected from smooth metallic plates, and then to fall on a thermo-electric pile. They obtained the following results with an incidence-angle of 50°:

Plated silver, well polished	0·97	Speculum-metal, freshly polished	0·855
Gilt steel, perfectly polished	0·97	" slightly dimmed	0·825
Plated gold	0·95	Platinum	0·83
Copper	0·93	Steel	0·825
Brass	0·93	Zinc	0·81
Varnished copper	0·86	Iron	0·77

The method of preparing the metal surfaces has an extremely slight influence on the reflecting power, provided the polish is always perfect.—The sum of the reflecting and radiating powers of silver (0·97 + 0·025) is very nearly = 1, and since the dispersion by silver is only extremely small, this result offers a confirmation of the equality of the powers of absorption and of emission.—The intensity of the heat-rays reflected from a glass surface increases considerably with the increase of the angle of incidence, and the absorption, and therefore also, the radiation, must suffer a corresponding diminution.

Reflection of Heat-rays.—Knoblauch(2) has, by means of comparative experiments with a mirror of black glass, and with one of steel, confirmed the proposition already put forth by Forbes, and by De la Provostaye and Desains, that the intensity of the reflected heat is augmented with the increase of the angle of incidence in the case of glass, and diminished in the case of metals. His experiments gave the following deflection of the multiplier-needle:

Angles of the heat-rays with the mirror	60°	50°	40°	30°	20°	10°
On black glass	10·0	10·0	11·0	15·1	28·1	43·0
On steel	56.0	55·0	54·5	50·0	48·0	43·0

The experiments of De la Provostaye and Desains, on the intensity of radiation at different angles of divergence, gave the following results:

(1) Phil. Mag. [3] XXXI, 69. (2) Pogg. Ann. LXXIV, 168.

Reflection of heat-rays.

Angles of divergence	0°	60°	70°	75°	80°
From lampblack . .	100	—	100	—	100
„ glass	90	83·6	75·01	65·3	54·44
„ white-lead paint .	100	94·6	83.9	—	65·9
„ red-ochre paint .	100	—	91·2	—	82·3
„ black paint . .	100	—	—	—	76

The proposition enunciated by Lambert, and also, in the opinion of Leslie, practically confirmed by his own experiments, that the intensity of the radiated heat is proportional to the sine of the angle of divergence, must be modified according to the results just adduced. Each of the above numbers would, according to Lambert's proposition, have been 100, since the magnitudes of the radiating surfaces are always inversely proportional to the sines of the angles of divergence. In the case of glass especially, there appears to be a remarkable anomaly, as indeed might have been inferred from the strength of the reflection at large angles of incidence, for whatever may be the governing law, the equality of the radiation and absorption being assumed, the sum of the reflection, the radiation, and the diffusion must be equal to 1.—The reader is referred to the memoir itself for some theoretical considerations, as well as for the whole of its second section, in which are given analytical expressions of the interchange of heat between a spherical shell of constant temperature, and a globular thermometer in its centre, and also of that between a thermometer, and a source of heat in a medium of constant temperature.—De la Provostaye and Desains(1) have also published a paper on the diffusion of heat from metallic surfaces.

Double Refraction, Polarization, Interference, and Inflection of Radiant Heat.—The double refraction of radiant heat has already been proved by Berard, Forbes, and Melloni, and its polarization by the same three authors and by Erman, however the perfect analogy between the behaviour of light and of radiant heat, in reference to refraction, polarization, interference, and inflection, has been first established by the extensive researches of Knoblauch, and by some experiments of De la Provostaye and Desains.

Knoblauch(2) directed sun-rays, reflected from a heliostat, upon the natural rhombic surface of a crystal of calc-spar, and received the rays which passed through it on a thermo-pile, whose surface formed a vertical strip of only $\frac{1}{4}$ᵐᵐ breadth. A deflection of 20°·5, a return to 5°, and a secondary deflection of 20°·75, unequivocally proved the double refraction of the heat. The distance of the extreme borders

(1) Compt. Rend. XXVI, 212; Pogg. Ann. LXXIV, 117.
(2) Pogg. Ann. LXXIV, 1.

Double refraction, polarization, interference, and inflection of radiant heat.

of the two heat-images was altered, if the calc-spar was made to revolve in a plane perpendicular to the heat-rays. It was necessary to turn it through 90°, to cause their distance to increase from its minimum to its maximum. On the rotation of the calc-spar, one of the pencils of rays (that of extraordinary refraction) moved round the other, (of ordinary refraction,) which remained stationary. The intensity of the two pencils was equal. None of the phenomena of double refraction appeared, if a plate, slit off from the crystal perpendicularly to its axis, was employed.

Knoblauch(1) obtained the polarization of heat by reflection, by throwing sun-rays from a mirror of black glass or of steel, through a Nichol's prism.—Various angles of incidence being employed, it resulted, that the perfection of the polarization increased at first, when the angle formed by the heat-rays with the mirror was small, and afterwards diminished. The best polarization appeared, when this inclination was, with the glass mirror 35°, with the steel about 15°. The maximum, in the first case, amounted to 74 rays polarized, out of 100 reflected; in the latter to only 34.

Knoblauch(2) tested the polarization of heat by simple refraction in three different ways. The subjoined table represents in columns I the results obtained, when a set of parallel glass plates served as the polarizer, and a similar set as the analyzer; in II, when a Nichol's prism was employed to analyse; in III, when a Nichol polarized, and a set of glass plates analysed.

Angle of incidence of heat-rays.	Of 100 rays, were polarized, by use of											
	3 plates.			6 plates.			9 plates.			12 plates.		
	I.	II.	III.	I.	II.	III.	I.	II.	III.	I.	II.	III.
0°	0	0	0	0	0	0	0	0	0	0	0	0
20°	0	10	9	0	17	13	0	30	20	13	44	50
40°	0	22	25	13	53	38	25	63	51	50	70	69
60°	21	36	47	53	81	71	76	96	92	100	100	100

The polarization, by simple refraction, is therefore the more perfect; Firstly, the greater the angle of incidence, the number of glass plates being constant, Secondly, the greater the number of plates, the incidence-angle being constant. The planes of polarization of reflected and of refracted heat are at right angles.

The polarization by double refraction has also been examined by

(1) Pogg. Ann. LXXIV, 161. (2) Ibid. 177.

Double refraction, polarization, interference, and inflection of radiant heat.

Knoblauch(1). Crossed tourmalines polarized 58 rays out of 100 of those that passed through the parallel plates. A Nichol's prism gave a very complete polarization; and this phenomenon is at the same time a new proof of the total reflection of heat-rays.—The two heat-images exhibited by calc-spar proved to be polarized in planes perpendicular to each other. A plate of calc-spar between Nichol's, parallel or crossed, presented with heat-rays, phenomena perfectly analogous to those of light. A closer examination showed farther, that the heat was unaffected as to its intensity and quality, in whatever direction it might pass through the calc-spar.

Knoblauch(2) proved the *inflection* of heat-rays, by preparing a linear heat-source with a heliostat and a cylindrical lens, from which he passed the rays through a narrow crevice, behind which he determined the field, over which the heat-rays were spread, by means of a linear thermo-pile. This field was always greater than that due to its propagation in straight lines. The difference was the more considerable, Firstly, the farther from the slit the measurement was taken; Secondly, the narrower the crevice through which the rays passed; Thirdly, the greater its distance from the source of heat.

Fizeau and Foucault(3) have proved the interference of heat-rays in the reflection-fringes; in the spectra with dark spaces, which are obtained by prismatic decomposition of the colours of crystalline laminæ in polarized light, and lastly, in the diffraction-fringes produced by a rectilinear edge. The interference-stripes of heat coincide with those of light, and appear in the whole extent of the heat-spectrum. These physicists made use, for their experiments, of an extremely delicate alcohol thermometer, whose globular bulb was of no greater diameter than $1^{mm}\cdot1$, on which, however, 1^0 C. occupied a length of 8^{mm}, so as to admit of the reading off even $\frac{1}{400}$th of a degree. In passing through the middle reflection-fringes, the thermometer indicated 20·9; 35·9; 20·0 divisions.

(1) Pogg. Ann. LXXIV, 177.
(2) Ibid. 9; Instit. 1848, 139.
(3) Compt. Rend. XXV, 447, 485; Pogg. Ann. LXXIII, 462.

KINETICS.

(SCIENCE OF MOTION.)

On Forces in general.—Grove has published a pamphlet(1) "On the Correlation of Physical Forces," of which a summary, translated by Louyet, has been communicated to the Belgian "Revue Scientifique," from which it has passed into the "Institut"(2). Its leading notion, that each of the following forces, motion, heat, electricity, light, magnetism, and chemical attraction, can be converted into all of the others is not altogether new, and perhaps the author has not supported his position with all the materials which were at his disposal; and there still remains a difficulty in representing the facts connected with latent heat as phenomena of motion. Grove thus describes an experiment devised by himself to prove the conversion of light into the other modes of force. A prepared Daguerreotype plate is enclosed in a box, filled with water, having a glass front with a shutter over it: between this glass and the plate is placed a gridiron of silver wire; the plate is connected with one extremity of a galvanometer coil, and the gridiron of wire with one extremity of a Breguet's helix; the other extremities of the galvanometer and helix are connected by a wire, and the needles brought to zero. As soon as, the shutter being removed, a beam of either daylight or the oxy-hydrogen light falls on the plate, the needles are deflected, proving that chemical action, electricity, magnetism, heat, and motion, are elicited by the light.—Among some philosophical considerations of the essential nature of physical causes, and of the imperfection of technical nomenclature, this essay contains some unusual notions, for instance, concerning the cause of light, which Grove attributes, without recourse to an ether, to the vibration of material particles, an opinion, which is scarcely supported by the instance adduced of the dependence of the optical properties of substances on their structure, and would entail the difficult inference that space must be filled with material particles. Grove very justly remarks, that the next problem connected with the correlation of the physical forces must be the numerical determination of their equivalents. Towards the solution of this we have as steps, the expression

On forces in general.

(1) On the Corr. Phys. Forces, the substance of a course of lectures delivered in the London Institution, Lond. 1846; Phil. Mag. [3] XXXI, 67.

(2) Institut. 1848, 154, 162, 169, 176.

On forces in general. of the mechanical equivalent of heat by Joule, and of the relations of the magnetic forces by Gauss and Weber, and the measurement of the electro-chemical equivalent of water by Weber.

Researches in a similar direction have been published by Haughton(1) and by Goodman(2). Matteucci(3) has instituted a series of experiments, which seemed to entitle him to conclude, that the imponderables—heat, light, and electricity,—are developed in chemical processes in quantities independent of each other, so that the amount of the first sustains no alteration by the simultaneous appearance of a second or third of them.

Theory of Matter.—Ellis(4) has communicated some remarks to the Cambridge Philosophical Society, in which, acknowledging that chemical processes cannot, as yet, be explained mechanically, he suggests a new principle of causation, which he calls $(\text{force})^2$, bearing the same relation to force that force does to velocity; the analogy of which leads him further to the kinematical conception of $(\text{force})^3$, ... $(\text{force})^n$, &c.

Equilibrium of Solids.—De Saint-Venant(5) remarks, in a treatise on the equilibrium of solid bodies, that the formulæ of molecular mechanics have hitherto always been founded on the hypothesis, that the distance of two molecules in magnitude, as well as in direction, is subject only to very small alterations. If metallic ribands, or rods, are bent so as to bring their ends into contact, or are wound spirally, this hypothesis is no longer admissible. Saint-Venant developes new formulæ, on the assumption, that the ratio of the distances of two molecules, before and after the displacement, differs very little from 1. Firstly, Let d_x, d_y, d_z, be the increments in length of three material lines, which lie perpendicularly to each other, in a point M of the material body, and parallel to the coordinates x, y, z; and Secondly, let g_{yz}, g_{xz}, g_{xy}, be the small increments of the right angles; then for a displacement ξ, η, ζ:

$$dx = \frac{d\xi}{dx} + \frac{d\xi^2 + d\eta^2 + d\zeta^2}{2dx^2}; \text{ and}$$

$$g_{yz} = \frac{d\eta}{dz} + \frac{d\zeta}{dy} + \left(\frac{d\xi\, d\xi}{dy\, dz} + \frac{d\eta\, d\eta}{dy\, dz} + \frac{d\zeta\, d\zeta}{dy\, dz}\right)$$

(1) Phil. Mag. [3] XXX, 437, 502.

(2) Transactions of Manchester Lit. and Phil. Soc. Vol. VIII; Phil. Mag. [3] XXXII, 172.

(3) Arch. Ph. Nat. IV, 381.

(4) Phil. Mag. [3] XXXIII, 393.

(5) Compt. Rend. XXIV, 260.

and in these expressions the second members vanish under the hypothesis before laid down, that ξ, η, ζ are small. The increment of another right line, which makes angles α, β, γ with the co-ordinate axes is Equilibrium of solids.

$$D = d_x \cos^2\alpha + d_y \cos^2\beta + d_z \cos^2\gamma + g_{yz} \cos\beta \cos\gamma + g_{xz} \cos\alpha \cos\gamma + g_{xy} \cos\alpha \cos\beta.$$

Saint-Venant has deduced from this formula results for some simpler cases.—Concerning the resistance of torsion, offered by a prism of rectangular section, Saint-Venant remarks, that, formerly, this had been falsely stated as proportional to the moment of *inertia* of the section. He adds, that Cauchy had already found that for equal moments of inertia, the resistance to the torsion was less, the more unequal the sides of the section, and also, that the section which before had been a plane, became warped by the torsion, like the sails of a windmill, being still bounded by right lines. Saint-Venant now finds, that the plane section suffers yet a further flexure, so that the curved surface stands at right angles to the four spirally twisted edges, and that the bounding edges are curved. An experiment with rods of caoutchouc confirmed the theoretical result. With this likewise agree the experiments of Duleau on the difference of resistance, in cylindrical, and in square-based prismatic rods, with the same moments of inertia of section. Let 2 h and 2 i be the sides of an elongated parallelopipedon, let $G = \frac{2}{3}$ E, (E being the coefficient of elasticity), (*G coëffic. d'élasticité de glissement*), and lastly, let d be the angle of torsion for the unit of length; then, according to Saint-Venant(1) the moment of torsion

$$M = \frac{16}{3} G \cdot dhi^3 - Gdi^4 \frac{1024}{\pi^5} \left\{ \frac{1 - e^{-\frac{\pi h}{i}}}{1 + e^{-\frac{\pi h}{i}}} + \frac{1}{3^5} \frac{1 - e^{-\frac{3\pi h}{i}}}{1 - e^{-\frac{3\pi h}{i}}} \right.$$

when h = i, then the prism has a square base; and

$$M = 0{\cdot}841 \cdot \frac{8\,Gdh^4}{3}$$

when i is very small in respect to h:

$$M = \frac{16}{3} Ghdi^3$$

as also Cauchy had already found.—A cylinder with circular base,

(1) Compt. Rend. XXIV, 485.

Equilibrium of solids.

whose section has the same moment of inertia, as the prism in the first mentioned case, presents a moment of torsion $M = \frac{8}{7} G\, d\, h^4$. While the calculation gives a ratio 0·841, it appears from the experiments of Duleau on iron rods to be 0·85, from those of Savart on copper rods 0·82.

Saint-Venant(1) calculates the moment of torsion, for a cylinder with elliptic base,

$$M = G\, d\,.\, \frac{4\, \mu\, \mu'}{\mu + \mu'}, \text{ where } \mu' = \frac{\pi}{2} h\, i^3, \text{ and } \mu' = \frac{\pi}{2} h^3\, i,$$

h and i being the axes of the ellipse. He finds, that the elliptic sections assume by the torsion the form of an hyperbolic paraboloid.

On the Elasticity and Compressibility of Solids.—The theory of elasticity leads to some results which are especially suited for experimental confirmation. Thus, for instance, the proposition that if a rod or cord is slightly increased in length by a force of traction, it also increases in volume in such a manner that the increment of the unit of volume amounts to half as much as that of the length-unit. Wertheim(2) finds the experimental corroboration of this proposition by Cagniard-Latour to be insufficient; experiments with rods of caoutchouc, as well as with cylindrical tubes of brass and of glass, (whose alteration in volume was measured in capillary tubes cemented into the top,) have shown the increase of the volume-unit to be nearly equal $\frac{1}{3}$ of that of the unit of length. Let π be the force of the thrust or strain, ε the linear extension in the direction of this force, v the alteration of volume, k and K the coefficients of linear and cubic compressibility or expansibility, then the fundamental hypothesis of Cauchy, concerning the elastic action, is expressed by the equation $\pi = k\,.\,\varepsilon + K\,.\,v$. Hence, for a cylinder, on whose convex surface no force is acting, while a thrust or strain bears on its base surfaces, Cauchy deduces the equation $v = \frac{k}{k + 2\,K}\,\varepsilon$, and if according to the result of the experiments, we make $v = \frac{1}{3}\,\varepsilon$, this gives $k = K$, therefore $\pi = k\,(\varepsilon + v)$. If we substitute these values in the general equations of equilibrium and motion, we now obtain, for certain special cases, formulæ different from those based upon the former hypothesis, that $v = \frac{1}{2}\,\varepsilon$, or $k = 2K$. These formulæ,

(1) Compt. Rend. XXIV, 847.

(2) Ann. Ch. Phys. [3] XXIII, 52; Compt. Rend. XXVI, 206; Pogg. Ann. LXXIV, 150.

applied to Regnault's experiments on the cubic compressibility of shells of solid matter, give the following confirmation : Equilibrium of solids.

Shells.	Cubic compressibility for 1 atm. on 1 square centim.	Coefficient of elasticity in kilogr. for 1 square millim. after		
		the old formula.	the new formula.	the increase of length.
Copper globe	0·0000013377	11550	10266	10519
Brass globe	0·0000014788	10417	9287	9277
Glass cylinder with hemispherical ends. . .	0·0000022897	6748	5998	6010

The relation $v = \frac{1}{4} \epsilon$ combined with Cauchy's mathematical deductions, leads to an equation, which is satisfied by the assumption, that the molecular attraction is inversely proportional *to the 14th power of the distance of two molecules.* Lastly, too, it follows, that the velocity of sound in an infinite mass is to that in a thread of the same substance as $\sqrt{\frac{3}{2}}$: 1.

Elasticity and Solidity of different Glasses. — Chevandier and Wertheim(1) have measured the elasticity and solidity of various sorts of glass. Pieces of 1—2 metres in length, cut from rods which had been drawn out to 10—12 metres, gave for the velocity of sound very discrepant results. Indeed they were never concordant until the rods were annealed and very accurately worked into prisms of square section. Window-glass gave a sound-velocity between 16·58 and 16·76; plate-glass 15·70—16·02. Besides these two sorts, flint-glass and crystal-glass were also examined. The following table contains some of their results.

	Coefficient of elasticity, from the sound-velocity.	Cohesion in kilogrm for 1 square millim. of section.
Window-glass	7917	1·763
Plate-glass	7015	1·400
Colourless flint-glass	6890	1·002
White or coloured crystal-glass . .	5477	0·665

The density of the glasses increases somewhat by annealing, as also does the coefficient of elasticity. The measurement of the elongation gave for the latter smaller values than did the measurement of the number of vibrations. The comparative elasticities of the glasses are parallel with their relative hardnesses. These properties are least

(1) Ann. Ch. Phys. [3] XIX, 129, 252.

Elasticity and solidity of different glasses.

in the glasses that contain lead; in such as contain no lead they are weaker if they contain but little lime and a comparatively large proportion of silicic acid.

Mechanical Properties of Woods.—Chevandier and Wertheim(1) have also again tested the mechanical properties of the woods in ordinary use, which, since the time of Muschenbroek, have been so often examined; and this, by comparing not only the several species, but also the same sorts of wood at different ages; the upper and lower parts of the trunks; the exterior and the inner parts of the timbers, in the form of thin laths and planks, as well as of beams, in the green state and in various stages of dryness. Rods of square section, 10^{mm} in thickness and 2^{m} in length, were prepared, being cut in the direction of the fibres, and the velocity of sound in them was determined by the longitudinal vibrations, their elasticity from their increase in length, and their cohesion by loading them to the point of rupture. Small rods were cut in planes perpendicular to the fibre-grain, (in directions radial and tangential to the rings of growth,) and their elasticity and sound-velocity were measured by the lateral vibrations. It was thus again established, that the coefficients of elasticity, as deduced from the vibrations, come out higher than those derived from the elongations. For the special results and inferences we must refer to the memoir itself, from which we select only the following:

Names of the woods.	Density.	Sound-velocity.			Coefficients of elasticity.			Cohesion.		
		L.	R.	T.	L.	R.	T.	L.	R.	T.
Acacia . .	0·717	14·19	—	—	1261·9	—	—	7·93	—	—
Fir . . .	0·493	13·96	8·05	4·72	1113·2	94·5	34·1	4·18	0·220	0·297
Hornbeam .	0·756	11·80	10·28	7·20	1085·7	208·4	103·4	2·99	1·007	0·618
Birch . . .	0·812	13·32	6·16	9·14	997·2	81·1	155·2	4·30	0·823	1·063
Beech . . .	0·823	10·06	11·06	8·53	980·4	269·7	159·3	3·57	0·885	0·752
Pedunculated oak . . .	0·808	—	—	—	977·8	—	–	6·49	—	—
Holm-oak .	0 872	11·58	9·24	7·76	921·3	188·7	129·8	5·66	0.582	0·106
Pine [P. sylv.]	0·559	10·00	8 53	4·78	561·1	97·7	28·6	2·48	0·256	0·196
Sycamore . .	0·692	13·13	9·02	6·85	1163·8	131·9	80·5	6·16	0·522	0·610
Ash . . .	0·697	11·05	8·39	7·60	1121·1	111·3	102 0	6·78	0·218	0·408
Alder . . .	0·601	13·95	8·25	6·28	1108·1	98·3	59·1	4·54	0·329	0·175
Aspen . . .	0·602	15·30	9·72	5·18	1075·9	107·6	43·4	7·20	0·171	0·414
Maple . . .	0·674	12·36	9·26	6·23	1021·4	157·1	72·7	3·58	0·716	0·371
Poplar . .	0·477	12·89	8·44	6·32	517·2	73·3	38·9	1·97	0·146	0·214
Elm . . .	—	—	8·56	6·11	—	122·6	63·4	—	0.315	0·366

(1) Compt. Rend. XXIII, 683; Pogg. Ann. Ergänz. Bd. II, 481; also a Report thereon by Brogniart, Regnault, and Poncelet, Compt. Rend. XXIV, 537.

L refers to the rods cut lengthwise with the grain; these were dried to 20 per cent of moisture; R to those cut in a direction radial, and T to those tangential, to the annual rings. Mechanical properties of woods

Elasticity and Cohesion of the Tissues of the Human Body.— Wertheim(1) has further examined the elasticity and cohesion of the bones, sinews, muscles, nerves, arteries, and veins of the human body. He found the cohesion in kilogrammes for 1 square millimetre section.

Tissues.	Sexes.	Years of age.	Specific gravity.	Coefficient of elasticity.	Cohesion.
Bone, Femur	F.	21	1·968	2181	6·87
„ Tibia	F.	21	1·910	2710	10·26
„ Femur	M.	30	1·984	1819	10·50
„ Tibia	M.	30	1·997	2059	15·03
„ Femur	F.	60	1·849	2421	6·40
„ Tibia	F.	60	1·799	—	3·30
„ Femur	M.	71	1·987	2638	7·30
„ Tibia	M.	71	1·947	—	4·34
Tendon of plantaris longus	F.	21	1·115	164·71	10·38
„ „ „	M.	35	1·125	139·12	4·91
„ „ flexor pollicis longus	M.	35	1·132	128·39	—
„ „ „ „ „ slightly dried	M.	35	1·132	183·44	—
„ „ „ „ „ perfectly dried	M.	35	1·132	186·85	4·11
„ „ „ „ „ „	M.	40	1·121	134·78	7·10
„ „ „ „ „ „	F.	70	1·114	169·21	5·61
„ „ „ „ „ „	M.	74	1·105	200·50	5·39
Muscles, sartorius	M.	1	1·071	1·271	0·070
„ „	F.	21	1·049	0·857	0·040
„ „	M.	30	1·058	0·352	0·026
„ „	F.	60	1·010	—	—
„ „	M.	74	1·045	0·261	0·017
Nerves, nervus popliteus internus	F.	21	1·038	—	0·769
„ nervus ischiaticus	F.	21	1·030	10·053	0·900
„ „	M.	35	1·071	23·943	0·963
„ tibialis posticus	M.	35	1·040	—	1·959
„ „ „	M.	40	1·041	26·127	1·300
„ nervus ischiaticus	F.	60	1·028	13·517	0·800
„ nervus cutaneus suræ	F.	70	1·052	23·878	3·530
„ nervus ischiaticus	M.	74	1·014	14·004	0·590
„ tibialis posticus	M.	74	1·041	32·417	—
„ nervus saphenus externus	M.	74	1·050	—	—
„ dried	M.	74	1·129	164·20	9·46
Artery, Femoral	F.	21	1·056	—	0·1103
„ „	M.	30	1·014	0·052	0·1660
„ „ cartilaginous	F.	70	1·085	—	0·1070
Veins, vena femoralis	F.	21	1·055	0·844	0·0969
„ vena saphena interna	F.	21	1·048	—	0·3108
	F	70	1·019	0·883	0·1490

(1) Ann. Ch. Phys. [3] XXI, 385.

Elasticity and cohesion of the tissues of the human body.

From Wertheim's experiments it appears,—that, 1stly, the specific gravity of tendons, muscles, and veins decreases with the age of the subject, while, on the contrary, that of the arteries increases, in consequence of an ossification of their walls; 2ndly, the bony structures become elongated almost in exact proportion to the strain upon them, as do inorganic bodies and woods, while, on the contrary, the soft parts of the body are elongated at first in a greater ratio, and only under a greater weight does this relation become one of direct proportion; 3rdly, the coefficients of elasticity of the bones, tendons, and nerves, seem to increase with the age, those of the muscles, however, to diminish considerably; 4thly, the cohesion of all the tissues decreases with increasing age; 5thly, the nervous trunks, have, for equal sections, less solidity than their branches, which again have less than their fibres, so that the solidity of nerves seems to increase as their thickness diminishes; 6thly, if the several tissues are arranged according to the magnitude of their coefficients of elasticity, or according to their cohesion, in either case, the following series is obtained, bones, tendons, nerves, muscles, veins, arteries; 7thly, the elasticity and cohesion of each and all are increased by drying. The experiments were made three or four days after death. For fresh muscles, the coefficient of elasticity seems to be about 1·15 times, and the cohesion 1·44 times, greater than the numbers given in the table.

Relation between the Elasticity and Fusion-Heat of Solids.— Person(1) remarks, that a close approximation to a proportionality is recognised as existing between the coefficients of elasticity of many solid bodies and their latent fusion-heat, as shown by the comparison of zinc with tin, with lead, and with bismuth. He adds, that we have still greater reason to infer such a relation as existing between the latent fusion-heat and a function of the coefficient of elasticity, expressing the power that is requisite, so far to alter the cohesion of the molecules, in the unit of weight, as is necessary to induce the transition from the solid to the liquid state. Taking a cube of the unit-weight (1 grm.), and σ as the elongation of its side, when the cohesion is resolved; assuming farther the straining force s to be proportional to the elongation up to this point, then is the force expended $3\int_0^{\sigma} ds \, . \, ks = \frac{3}{2} k \sigma^2$. Let p be the specific gravity, q the coefficient of elasticity, 1000 q the number of

(1) Ann. Ch. Phys. [3] XXIV, 265; Compt. Rend. XXVII, 258; Instit. 1848, 299.

grammes necessary to stretch a rod of 1 square millimetre section to twice its length; then $\frac{1}{p}$ is the volume of the cube, $\frac{100}{p^{\frac{2}{3}}}$ the section in square millimetres, and $\frac{100000\,q}{p^{\frac{1}{3}}}$ grm. produce an elongation of 1 c.m. (the assumed unit of length).—Let S be the value of σ, which corresponds to the unit of length, then $\sigma = \frac{S}{p^{\frac{1}{3}}}$, and the power employed $= \frac{4{\cdot}5\,q\,S^2}{p}$ in kilogrammetres(1). For two metals then, we have $\frac{q\,S^2}{p} : \frac{q_1\,S_1{}^2}{p_1} = l : l_1$, where l represents the latent fusion-heat. Person found that the results agree with those of observation, if we assume the equation $\frac{S^2}{p + 2\sqrt{p}} = \frac{S_1{}^2}{p_1 + 2\sqrt{p_1}}$, from which we obtain the formula $q\left(1 + \frac{2}{\sqrt{p}}\right) : q_1\left(1 + \frac{2}{\sqrt{p_1}}\right) = l : l_1$. This formula is confirmed in the cases of zinc and of lead, (5·28, 5·23); for tin and lead (2·42, 2·65); for zinc and d'Arcet's alloy (3·92, 3·68); likewise for cadmium and silver. The coefficients of elasticity of these two metals were determined by Wertheim with very great accuracy. Calculation gives the latent fusion-heat for cadmium 13·52; Person's measurements gave 13·66. For silver the formula gives 20·38, experiment 21·07.

Relation between the elasticity and fusion-heat of solids.

Equilibrium of Liquids. Their Compressibility.—In the older experiments on the compressibility of liquids there is a want of accuracy, arising from this, that the correction for the compressibility of the walls of the vessel was founded on arbitrary assumptions. Regnault(1), therefore, arranged his experiments on the compressibility of water in glass and brass vessels, as well as on that of mercury in a glass piesometer, in such a manner, that the alteration in volume of the substance of the containing vessel could be simultaneously deduced from them. The compression was effected, not by a screw, but by compressed air, which presents the great advantage, that the power applied can be graduated with the greatest nicety, so that a permanent change of form in the piesometer is not so much to be feared. In five successive experiments, the

(1) 1 kilogrammetre = the force required to raise 1 kilogrm. through a height of 1 metre.

(2) Relation, &c. (p. 52), 429.

Equilibrium of liquids. Their compressibility.

piesometer was exposed, as follows: 1stly, without and within, to the atmospheric pressure; 2ndly, without, to a stronger, within, to the atmospheric pressure; 3rdly, without and within, to an increased pressure; 4thly, without, to the atmospheric, within, to the higher; and 5thly, to the same pressure again as in the first case.—Hence, three equations were always obtained, of which two served to determine the compression of the liquid and of the vessel, and the third to check the results. The formulæ are developed by Lamé, for 1stly, a spherical shell; 2ndly, a cylindrical shell with plane; and 3rdly, a cylindrical shell with spherical ends. Let μ and k represent the cubic compressibility of the liquid and the solid; V and U the volumes of the fluid contained in the piesometer of the 1st and 2nd forms respectively; N and M, the ratios of these volumes to that of the solid mass of the piesometer, the apparent diminution of V and U by an excess of pressure from within represented by P; and their apparent increase respectively under simple external, and under external and internal, pressure; then, according to Lamé:

For a spherical shell.	For a cylindrical shell with plane ends.	For a cylindrical shell with spherical ends.
$kP = \frac{1}{V}\left\{\frac{4\vartheta'}{9(N+1)}\right\}$	$kP = \frac{1}{U} \cdot \frac{3\vartheta'}{8(M+1)}$	$kP = \frac{\vartheta'}{\frac{3}{8}(M+1)U + \frac{3}{4}(N+1)V}$
$\vartheta'' = \vartheta - \vartheta'$	$\vartheta'' = \vartheta - \vartheta'$	$\vartheta'' = \vartheta - \vartheta'$
$\mu P = \frac{1}{V}\left\{\vartheta'' + \frac{4\vartheta'}{9(N+1)}\right\}$	$\mu P = \frac{1}{U}\left\{\vartheta'' + \frac{3\vartheta'}{8(M+1)}\right\}$	$\mu P = \frac{1}{U+V} + \frac{\vartheta'}{\frac{3}{8}(M+1)U + \frac{3}{4}(N+1)V}$

For water Regnault obtained the following results; under the pressure of 1 atmosphere:

	In a copper globe.	In a brass globe.	In a glass cylinder, with spherical ends.
μ	0·000047709	0·000048288	0·000046677
k	0·000001317	0·000001440	0·000002368

The compressibility of mercury under 1 atmosphere was found = 0·000003517, under a column of mercury of 1^{m} height = 0·000004628.—Incidentally to these experiments, Regnault found that a pressure of 10 atmospheres, acting suddenly on water, did not evolve so much heat as to raise its temperature $\frac{1}{50}{}^{\circ}$.

Grassi(1) has measured, in Regnault's laboratory, and by his method, the compressibility of some other liquids. He found for,

(1) Compt. Rend. XXVII, 153; Dingl. pol. J CX, 31.

Equilibrium of liquids. Their compressibility.

Distilled water deprived of air.

Temp.	Compressibility under 1 atmos.
0°	0·0000505601
10°·8	0·0000487053
13 ·4	0·0000483777
15 ·5	0·0000477446
25 ·9	0·0000458125
34 ·8	0·0000455727
43 ·0	0·0000444137
53 ·3	0·0000443355

	Compressibility under 1 atmosphere.
Solution of NaO, NO_5	0·0000306565
„ „ NaO, CO_2	0·0000303294
Artificial sea-water	0·0000445029
Saturated solution of CaCl	0·0000209830

	Pressure in metres.	Compressibility.
Ether	2^{m}·589	0·00011137
„	5915 ·000	0·00013073
Alcohol	1 ·748	0·0000824516
„	7158 ·000	0·00008587

Colladon and Sturm had found, that the compressibility of alcohol and of ether diminished under increased pressure. The experiments of Grassi indicate the contrary; chloroform and acetic ether behave similarly.

Equilibrium of Gaseous Fluids. Their Compressibility.—The experiments which have been made to test the truth of the law of Mariotte, as applied to cases of high pressures, involve one common source of inaccuracy, which arises out of the considerable influence of any error in the determination of the volume, when gases have been compressed under high power into a very small space. Regnault(1), therefore, so arranged the apparatus which he used for this purpose, that, in successive experiments, the same space of the manometer-tube could be filled under continually increasing pressures, and that the volume need be diminished only one half under each increase of pressure. The volumes 1 and ½ were marked on the manometer by two strokes. A full description of the apparatus, which was set up in the *Collège de France,* in a tower built specially for Savart's hydraulic experiments, will be found *op. cit.* pp. 341—367.—None of the gases examined followed, even under low pressure, the law of Mariotte. Atmospheric air, nitrogen, and carbonic acid are more compressible, and hydrogen less so, than would accord with the expression for Mariotte's law $\frac{\quad}{V_1} \cdot \frac{P_0}{P_1} - 1 = 0$. If the property of the first of these gases is explained by referring it to an imperfectly gaseous state; then for hydrogen the absurdity comes out, of a gaseity more than gaseous. Regnault thinks, that $\frac{V_0 \cdot P_0}{V_1 \cdot P_1} - 1$ is to be considered as a rather complicated function of the pressure and temperature, whose form it would be very difficult to discover by experimental methods alone. He calculates formulæ of interpolation according to the form

(1) Relation, &c. (see p. 52), 329.

Equilibrium of gaseous fluids. Their compressibility.

$\frac{r}{m} = 1 + A(m-1) + B(m-1)^2$, where m represents the ratio of condensation, r the ratio of pressures, and the coefficients A and B the following values:

	Atmospheric air.		Nitrogen.		Carbonic acid.		Hydrogen.	
	Sign.	Log.	Sign.	Log.	Sign.	Log.	Sign.	Log.
A.	—	$\bar{3}$·0435120	—	$\bar{4}$·8389375	—	$\bar{3}$·9310399	+	$\bar{1}$·7381736
B.	+	$\bar{5}$·2873751	+	$\bar{6}$·8176020	—	$\bar{6}$·8624721	+	$\bar{6}$·9250787

From these formulæ we get, for the ratio of condensation m, the subjoined pressures:

m.	Atmospheric air.	Nitrogen.	Carbonic acid.	Hydrogen.
1	1·000000	1·000000	1·00000	1·000000
2	1·997828	1·998631	1·98292	2·001110
3	2·993601	2·995944	2·94873	3·003384
4	3·987432	3·991972	3·89736	1·006856
5	4·979410	4·968760	4·82880	5·011615
6	5·969748	5·980350	5·74296	6·017676
7	6·958455	6·972791	6·63985	7·025102
8	7·945696	7·964112	7·51936	8·033941
9	8·931573	8·954361	8·38152	9·044244
10	9·916220	9·913590	9·22620	10·056070
11	10·899724	10·931833	10·05315	11·069454
12	11·882232	11·919120	10·86321	12·084456
13	12·863838	12·905516	11·65541	13·101144
14	13·814670	13·891052	12·43018	14·119504
15	14·824845	14·875770	13·18695	15·139650
16	15·801480	15·859712	13·92608	16·161632
17	16·783675	16·942920	14·64771	17·185470
18	17·762562	17·825436	15·35148	18·211230
19	18·741258	18·807321	16·03733	19·238963
20	19·719880	19·788580	16·70540	20·268720

Kinetics in general.—Of the contributions on various subjects, to the general literature of Kinetics, we adduce the following:—The integration of the differential equations of the motion of a material point, as well as of the general equations of motion, by Serret(1), and by Sturm(2); On the principle of least action, and its applicability, by Bonnet(3); Remarks on analogy in mechanics, by Bertrand(4); On the alteration of the arbitrary constants in the problems of dynamics, by Ostrogradsky(5); A paper on the sym-

(1) Instit. 1848, 173, 183.
(2) Ibid. 190.
(3) Ibid. 184.
(4) Compt. Rend. XXV, 163.
(5) Petersb. Acad. Bull. VII, 113.

bolical equation of vibratory motion in an elastic medium, whether crystallized or uncrystallized, by O'Brien(1); A calculation, according to the Newtonian law of gravitation, of the force by which the molecules are kept together, and by which they are brought together, on precipitation from solution, by Seguin(2); On the motion of a system of particles, of which each consists of several molecules, by Cauchy(3). Ettingshausen(4) gives an immediate derivation of the differential equations of infinitely small motions of a homogeneous system of molecules, from the general equations of infinitely small displacements of the centres of gravity of the molecules of any one system.

Kinetics in general.

Moments of Inertia.—Timmermanns(5) puts forth the following proposition concerning the theory of the moments of inertia. If the ellipsoid of the moments of inertia is constructed about every point of an axis which is passed through any body, then the axis will be the diameter of all these ellipsoids, and the diametric planes conjugate with it all pass through one right line, that of the direction of the impulse, through which no pressure is exerted on the axes.—This right line generally lies obliquely to the plane which passes through the axis and the centre of gravity. It is perpendicular thereto only when the axis is, relatively to one of its points, the principal axis of the moments of inertia. In the case of oblique position, an impulse exerts along the common line of intersection no pressure at all upon the axis, but produces an action in the direction of the axis itself.

Motion of Solid Bodies: of Projectiles.—Didion(6) publishes an extract from a treatise on the true path of projectiles. The analytical solution of the problem gave results, not in strict accordance with all the earlier observations, of which Didion gives a summary. Didion has, therefore, illustrated the theory of balistics by a new set of calculations, in which he assumes the resistance of the air as proportional to two terms, which contain the second and third power of the velocity. His results agree very accurately with the mean values of the measurements made in 1844 and 1846 at Metz. He accounts for the discrepancies observed in the ranges and in the paths of single shots by certain disturbing forces, which are stated to act together with gravitation, and with the resistance of the air, which, however, he fails to specify more clearly.

(1) Phil. Mag. [3] XXXI, 376.
(2) Compt. Rend. XXVII, 314.
(3) Ibid. XXIV, 414.
(4) Compt. Rend. XXIV, 801.
(5) Instit. 1848, 42.
(6) Compt. Rend. XXVII, 495; Instit. 1848, 143.

Coefficients of elasticity and rotary oscillations.

Coefficients of Elasticity and Rotary Oscillations.—The coefficients of clasticity, as deduced from the rotary oscillations, always came out less than those determined by direct observation. This is true of the experiments of Coulomb, calculated by Biot, as well as for those of Duleau, Savart, Bevan, and Giulio.—Wertheim(1) has altered the general equations of the equilibrium, and of the motion of elastic bodies, so that while the relation between the coefficients of elasticity and the longitudinal and lateral vibrations remain the same, that of these coefficients to the oscillations of torsion are modified. Let n and n′ be the number of longitudinal and torsional vibrations of the deepest tone, which is given by a rod fixed at one extremity; then, for a cylindrical rod, we have, according to Poisson's formulæ $\frac{n}{n'} = \sqrt{\frac{5}{2}} = 1·5811$; according to Wertheim's formulæ $\frac{n}{n'} = \sqrt{\frac{8}{3}} = 1·6330$.

Savart, by experiment, has found this ratio to be = 1·6668, Wertheim = 1·6309.

Kirchoff(2) communicates a note on the theory of equilibrium and of the motion of an elastic plate.

Motion of Liquids. Their Velocity of Flow from Narrow Tubes.—Poiseuille(3) has found, in some earlier researches on the velocity with which water and alcohol flow from narrow tubes, that this velocity is proportional directly to the pressure, and inversely to the length of the tube, provided that this length does not fall below a certain limit, which increases and diminishes with the diameter; while, for shorter tubes, the velocity rises more rapidly than the pressure. He found, farther, that all other conditions being the same, the quantity discharged is proportional to the fourth power of the diameter of the tube. Let the quantity of liquid flowing out be represented by Q, the pressure by a water-column of height H, the diameter of the tube by D, its length by L, then $Q = k \cdot \frac{H \cdot D^4}{L}$, where k is a coefficient dependent on the nature of the liquid, and which increases rapidly with the temperature. Poiseuille found, for water of the temperature t:

$$Q = 183·6724\,(1 + 0·0336793t + 0·0002209936t^2)\,\frac{H \cdot D^4}{L}$$

(1) Instit. 1848, 397; Ann. Ch. Phys. [3] XXV, 209.
(2) Compt. Rend. XXVII, 394.
(3) Mém. des Savans étrang. IX; Ann. Ch. Phys. [3] VII, 50.

The experiments with alcohol, and with mixtures of alcohol and water, gave the remarkable result, that alcohol flows more slowly than water; farther, that absolute alcohol of specific gravity 0·8000, and a mixture of 1 part, by weight, of alcohol with 17⅓ of water, having a specific gravity 0·9893, flowed with nearly equal velocity, while a mixture of almost equal parts by weight of the two liquids, having a specific gravity 0·9300, required double the time to escape. This, according to Rudberg, is the mixture of maximum condensation.

Motion of liquids. Their velocity of flow from narrow tubes.

Poiseuille convinced himself by experiment, that the velocity of the flow of liquids was equally altered by the admixture of substances soluble in them, whether they were conducted through solid tubes of glass or of metal, or through tubes of organic substances, as, for instance, the capillary tubes of animals: he then undertook(1), for the service of physiology, a detailed inquiry into the acceleration or retardation, to which the flow of water through narrow glass tubes is subject, when the salts, acids, and bases found in the liquids of the animal body are mixed with it in quantities as small as those in which they are there present. This *small* addition of foreign substances to the water distinguishes the experiments of Poiseuille from some similar ones instituted by Girard in 1817, in which these substances were employed in the proportions of ¼, ⅓, or even ½. The following tables contain Poiseuille's results. The salts are arranged according to their acids, which seem specially to influence the action.

The letters represent as follows — *B, C, D, E, F,* different tubes used in the experiments: L the length, and d the diameter, H the pressure in millimetres of water-column; T the temperature, P the parts of the substances, added to 100 parts of water; F the time of flow in seconds. The numbers in larger type are the times of flow of pure water.

Substances.	P.	F.	Substances.	P.	F.
B. L = 64; d = 0·24946; H = 1000; T = 11°·6.			*B.* L = 64; d = 0·24946; H = 1000; T = 11°·6.		
		568·3			
Iodide of potassium .	0·1	567·6			**569·5**
" " . .	0·2	566·7	Iodide of sodium . .	0·4	569·6
" " . .	0·4	565·6	" " . .	2·0	569·8
" " . .	0·8	563·5	" " . .	10·0	570·0
" " . .	2·0	557·6	" " . .	20·0	577·1
" " . .	10·0	530·4			**568·3**
" " . .	20·0	505·7	Iodine	satur.	568·7
" " . .	50·0	474·9	Iodide of iron . . .	2	568·2

(1) Ann. Ch. Phys. [3] XXI, 76.

Motion of liquids.
Their velocity of flow from narrow tubes.

Substances.	P.	F.
B. L = 64; d = 0·24946; H = 1000; T = 11°·6.		
Iodide of potassium .	10	568·5
Bromide of potassium .	0·4	565·8
" " .	2·0	560·0
" " .	10·0	537·6
T = 11°·2.		
		575·8
Nitrate of potassa . .	0·1	574·5
" " . .	0·2	573·5
" " . .	0·4	571·4
" " . .	1·0	561·5
" " . .	10·0	541·2
" " . .	20·0	533·3
Nitrate of ammonia .	1·0	569·1
" " . .	10·0	531·1
" soda . . .	1·0	575·9
" "	10·0	592·4
" lead . . .	1·0	577·8
" " . . .	4·0	582·9
" strontia . .	1·0	578·8
" " . .	4·0	586·7
" lime . . .	1·0	581·2
" " . . .	10·0	623·6
" magnesia .	1·0	583·2
" " . .	10·0	641·7
C. L = 37; d = 0·19495; H = 1370·8; T = 14°·2.		
		741·5
Nitrate of silver . . .	1·0	740·9
" " . . .	10·0	741·0
B. H = 1000. T = 11°·9.		
		565·0
Chloride of potassium .	1·0	560·8
" " . .	10·0	544·8
" ammonium	1·0	560·9
" " . .	2·0	556·5
" " . .	10·0	535·8
" sodium .	1·0	569·4
" " . .	10·0	640·3
" calcium .	1·0	571·2
" " . .	10·0	620·7
" magnesium	1·0	574·9
" " . .	10·0	646·8
B. H = 865·1.—T = 11°·2.		
		608·5
Protochloride of mercury		607·8
" saturated solution . . .	10	608·1
. . . . . .	20	607·9

Substances.	P.	F.
B. H = 100; T = 11°·2.		
		575·8
Hydrochlorate of morphine	1·25	589.8
" " strychnine	1·4	590·0
T = 12°·7.		
		554·0
Cyanide of potassium .	1·0	551·6
" " . .	4·0	518·8
" mercury .	1·0	558·6
" " . .	4·0	564·3
Pure serum	—	1014·5
In serum:		
Cyanide of potassium 1 : 100 ser.		998·7
" mercury 1 : 100 ser.		1025·3
T = 11°·2.		
		575·8
Sulphate of potassa .	1·0	578·9
" " . .	4·0	592·1
" ammonia .	1·0	582·0
" " . .	4·0	598·9
" soda . .	1·0	590·3
" " . .	4·0	606·1
" magnesia .	1·0	590·5
" " . .	4·0	630·1
" zinc . .	2·0	595·6
" iron (proto)	2·0	609·5
" morphine .	1·25	590·3
T = 12°·7.		
		575·8
Alum	1·0	592·4
"	4·0	632·4
Phosphate of potassa .	1·0	583·4
" " . .	4·0	602·7
" soda . .	1·0	588·6
" " . .	4·0	622·8
" ammonia.	1·0	590·2
" " . .	4·0	626·2
T = 11°·2.		
		575·6
Arseniate of potassa .	1.0	583·3
" " . .	2.0	590·8
" soda . .	1.0	588·0
" " . .	4.0	617·3
Bicarbonate of ammonia	1.0	580·6
" " potassa	1.0	580·4
" " soda .	1.0	589·8
Carbonate of ammonia.	1.0	583·8
" " . .	4.0	602·9
" potassa .	1.0	588·3
" " . .	4.0	617·0
" soda . .	1.0	592·5
" " . .	4.0	622·7

Motion of liquids. Their velocity of flow from narrow tubes.

Substances.	P.	F.
T = 11°·8.		
		566·2
Oxalate of potassa . .	1·0	571·1
" " . .	10·0	620·1
" ammonia .	1·0	571·2
" " . .	4·0	596·6
" soda . .	1·0	578·4
Binoxalate of potassa .	1·0	573·4
B. H = 858; T = 14°·1.		
		620·0
Acetate of lead . . .	1·0	633·1
" " . . .	4·0	653·5
B. H = 1000; T = 11°·1.		
		571·1
Citrate of iron . .	2·0	595·3
T = 11°·2.		
		575·8
Tartar emetic . . .	1·0	581·2
" " . . .	4·0	594·7
D. L = 105; d = 0·17; H = 1998·6; T = 12°·8.		
		123′38″
Acetate of ammonia .	2·0	122′25″
B. H = 1000; T = 11°·9.		
		564·7
Solid potassa . . .	2·0	579·4
" soda	2·0	611·4
Concentrated ammonia	10·0	628.7
" " .	pure.	725·4
T = 11°·2.		
		574·9
Hydriodic acid . . .	1·0	575·0
" " . . .	4·0	574·5
Nitric acid	1·0	573·9
" "	3·2	571·6
" "	8·2	573·3
T = 11°·8.		
		566·2
Solid iodic acid . . .	1·0	570·1
" " . . .	3·4	578·5

Substances.	P.	F.
E. L = 27; d = 0·1316; H = 2012·2; T = 10°.		
		499
Hydrocyanic acid . .	33·3	489
F. L = 70; d = 0·207; H = 2039·4; T = 10°.		
Pure serum		1448
100 water to 500 serum . .		1277
100 hydrocyanic acid to 500 serum		1278
100 hydrosulphuric acid to 500 serum		1266
B. H = 1000; T = 11°·6.		
		568·3
Hydrobromic acid . .	1·0	569·7
" " . .	7·2	571·4
Bromic acid	1·0	569·3
" "	3·2	570·5
T = 11°·2.		
		575·8
Hydrochloric acid . .	1·0	577·3
" " . .	2·0	579·5
" " . .	10·0	591·8
" " . .	20·0	604·3
Carbonic acid . . .	satur.	580·5
Artificial Selzer-water .	satur.	584·2
Solid oxalic acid . .	1·0	582·9
" " . .	2·0	590·6
" " . .	10·0	625·7
Solid phosphoric acid .	1·0	582·8
" " .	4·0	603·9
Acetic acid	1·0	585·5
" "	10·0	633·4
" "	pure.	1315·0
Solid citric acid . . .	1·0	586·0
" " . . .	10·0	682·1
Solid arsenic acid . .	1·0	586·3
" " . . .	4·0	618·0
Arsenious acid . .	1·0	578·6
Concentrated sulphuric acid	1·0	589·6
" " . .	pure.	14595·0
Solid tartaric acid . .	2·0	601·1

It is remarkable that strong doses of iodide of potassium, from the temperature 60° upwards, and nitrate of potassa from 40°, retard instead of accelerate. — Generally the flow is accelerated by iodide, bromide and cyanide of potassium, the nitrates of potassa and of ammonia, the chlorides of ammonium and of calcium, and acetate of ammonia.—These salts, then, so far as they do not act as poisons, must quicken the circulation of the blood; and, indeed, direct experiments on living horses have decided this for iodide

Motion of liquids. Their velocity of flow from narrow tubes.

of potassium and nitrate of potassa, and for chloride of ammonium and acetate of ammonia.—The other salts that were tested have no influence on the rate of flow.

All the bases retard the flow; and there seem to be only two acids, viz., the hydrocyanic and hydrosulphuric, that hasten it.

The farther inquiry of Poiseuille—whether the alterations produced by the admixture of other substances, in the density, in the capillary elevation, in the liquidity, and in the boiling point, whether the contraction attending their mixture, and whether the solubility, the liability to effloresce, and the tendency to crystallize, of the substances added, stand in any simple relation with the changes induced in the rate of flow,—elicited only negative results. A great number of mineral waters behave exactly as, according to the results here adduced, might have been expected from their saline contents. The quantity of salts diminishes the velocity of flow; but their action was greatly or entirely neutralized by the presence of hydrosulphuric acid, while, on the contrary, it was augmented by carbonic acid.

In the following tables the flowing-rates of such liquids as are used for beverages are compared, to which is added the influence of various bodies on the flow of the serum of blood. P here indicates the number of parts of the substances mixed with 1000 parts of the serum of ox-blood. The other letters correspond to those in the preceding table:

Substances.	P.	F.
B. H=800; T=18°.		
		602·0
Infusion of black tea(1)	pure.	611·5
Infusion of black and green tea in equal parts	pure.	614·0
Infusion of green tea .	pure.	618·2
" " " " .	10	604·3
" " " " .	20	606·5
" " " " .	33·3	608·3
" " " " .	100	610·6
" " " " .	300	615·8
B. H=1000; T=11·2		
		575·8
Madeira	pure.	1134·1
Sparkling wine . . .	"	1152·9
" (Sillery) . .	"	1462·8
Jamaica rum	"	1831·9

Substances.	P.	F.
B. H=1000; T=9°·2		
		611·2
Decoction of guaiacum.	pure.	612·4
" cinchona .	"	625·1
" " .	100	617·4
" marsh-mallow	pure.	646·5
" " .	100	634·5
B. H=1000; T=11°·2		
		575·2
Serum of ox-blood . .	P′.	1048·5
Sulphuric acid(2) . .	0·5	1057·4
" " . . .	1·0	1033·2
Citric acid	1·0	1035·5
" "	10·0	1140·2
Acetic acid	1·0	1041·3
" "	10·0	1070·7
Tartaric acid . . .	1·0	1041·1
" "	10·0	1233·5

(1) The tea was infused with 60 times its weight of boiling water.

(2) The acids were diluted previously, thus—the concentrated sulphuric with eight, the citric, acetic, and tartaric acids with four times their weight of water.

Substances.	P′.	F.	Substances.	P′.	F.
B. H=1000; T=14°.5.			Ether	2	1055·5
		535·2	Alcohol.	40	1223·4
Ether, pure		160·0	Ammonia	10	1000·1
„ 10 to 100 water .		773·3	„	20	981·6
Alcohol of 80° (Alcoholom.)		1184·5	Ether in serum with alcohol : : 4 : 1000 .		1434·1
Concentrated ammonia.		688·1	Ammonia : do. : : 4 : 100		1179·6
Ammonia with 10 parts of alcohol		1320·6	Ammonia : do. : : 7 : 100		1141·5
Serum of ox-blood . .		1029·0			
Ether	1	1038·8			

Motion of liquids.

Their velocity of flow from narrow tubes.

Ammonia runs more slowly than water, whose movement it retards; it accelerates, however, the flow of serum, pure as well as mixed with alcohol. Poiseuille considers that the effect of ammonia as an antidote, in the state of inebriation, is due to this action. This author has also examined the rate of flow of the blood: equal quantities of the following liquids were found to flow:

	Min.	Sec.
Serum, in	20	23
„ containing a small quantity of blood-globules, in .	21	17
Blood, freed from fibrine, in	68	47

Impulse from agitated Fluids on Immersed Bodies.—A paper by Saint Venant(1) has appeared on the theory of the resistance in fluids, according to which the paradox of d'Alembert, that a solid body immersed in an agitated fluid receives no impulse from it,—or that it offers no resistance to the fluid—is refuted, by due consideration of the friction between the fluid and the other body. For this paradox is substituted the proposition: a fluid actually in motion exerts on a body immersed in it, an impulse equal to the sum of the friction between the fluid and the solid, and of that between the liquid particles themselves.

De Caligny(2) describes the result of some experiments on the intermittence of a jet of water, which escapes either from an opening partially obstructed, or in the midst of several other surrounding jets.

Motion of Fluids generally.—Besides these, the following papers have been published on the motion of fluids: On the equation of continuity of fluid motion, by Hobson(3); On the motion of

(1) Compt. Rend. XXIV, 243; Cauchy's report on two papers by this author, mentioned Compt. Rend XXIV. 675.

(2) Inst. 1848, 127.

(3) Phil. Mag. [3] XXX, 104.

Motion of fluids generally. a fluid in a homogeneous medium, by Magnus(1); on the contraction of the water-jet, by Hagen(2).

The Syphon.—Person(3) points out that the problem of the syphon, which sucks when only its longer leg has been previously filled, is erroneously solved in Péclet's "Physics." Let a be the shorter, and c the longer of the vertical limbs, and b its horizontal limb,—then, according to Péclet, we must have $c > 2a + b$, but the true formula is $c > a + \frac{H(a + b)}{H - a}$, where H represents the height of a column of liquid equivalent to the pressure of 1 atmosphere.

Motion of Gaseous Fluids. Diffusion of Gases.—Blake(4) has made some theoretical remarks on the diffusion of gases, of which we do not give a fuller report, because they have led to results which are quite untenable, for instance, that the velocity and quantity of discharge from one vessel filled with gas, into the other, will be the same as in the case of diffusion into a vacuum, provided that the air in the second is less than half as dense as that in the first vessel.

Terrestrial Dynamics. Density of the Interior of the Earth.—If p represents the pressure at any point of the molten interior of the earth, and r the actual density at that point, Roche(5) deduces, from the equation $\frac{dp}{dr} = Ar + Br^2$, the law of the density $r = r_0(1 - \beta a^2)$, where a is the semi-diameter of the particular shell. $\beta = 0{\cdot}8$ satisfies the precession, as well as a flattening of the spheroid $= \frac{1}{300}$. The formula gives for a mean density 5·5, for that at the surface 2·1, for the middle point of the radius 8, and the centre 10·5, the flattening of the successive shells, increasing from $\frac{1}{570}$ at the centre to $\frac{1}{300}$ at the surface. Gravitation increases, on the hypothesis of the above law, from the surface up to a distance from the centre = 0·82 of the radius, at 0·65 it has the same value as at the surface, and then rapidly diminishes to the centre.

Attraction of the Terrestrial Spheroid.—Guiot(6) has written a paper on the attraction of the earth on points of its surface, and on the cause of its spheroidal form. He starts from an original proposition of his own, which he thus expresses:—At the pole of a sphere

(1) Berl. Acad. Ber. 1847, 305.
(2) Berl. Acad. Ber. 1847, 103.
(3) Compt. Rend. XXVII, 321; Instit. 1848, 294; Dingl. Pol. J. CX, 155.
(4) Sill. Am. J. [2] V, 78.
(5) Instit. 1848, 185.
(6) Compt. Rend. XXV, 195.

there is a very small zone, which exerts as strong an attraction, as would all the other parts of it together, if formed into a perfect spherical shell. Beyond, and reckoned from, this infinitely small zone, the attraction of any zone of constant thickness, is proportional to the sine of half of its generating arc.—Guiot calculates the pôlar flattening to be = $\frac{1}{285}$ from the data furnished by the observations made by Biot, Matthieu, Duperrey, Freycinet, Arago, and Sabine, with the pendulum. Attraction of the terrestrial spheroid.

Attraction of Spheroids.—Hennessy(1) has published a paper on the attraction of spheroids, in which he improves the demonstration given by Pontécoulant of an important theorem of Laplace.

Dependence of Gravity on the Latitude.—The calculation of the gravitation of the earth, or of the pendulum-length for a latitude λ, may be effected by the formula $l_\lambda = l + (l'' - l) \sin^2 \lambda$, where l is the length of the pendulum at the equator, l″ its length at the pole. Since, from this we obtain for $\lambda = 45^0$, $l_\lambda = \frac{l + l''}{2}$, which does not agree exactly with the truth, Babinet(2) prefers the more accurate formula: $l_\lambda = l + (l'' - l) \sin^2 \lambda - \left(\frac{l'' + l}{2} - l'\right) \sin^2 2\lambda$, where l′ is the length of pendulum for $\lambda = 45^0$.

Apparatus for determining the Density of the Earth.—Hearn(3) has made a communication to the Royal Society of London, on the disturbances introduced by diamagnetism into the determination of the mean density of the earth, by the use of Cavendish's apparatus.

Form of the Surface of the Sea.—Roche(4) makes some remarks on the irregularities, resulting from local attractions, in the surface of the sea.

Theory of Machinery: of Steam Engines.—Crelle(5) announces a full mathematical theory of steam-engines. He distinguishes in them the parts which serve for the generation of the power, as the furnace, boiler, chimney, hot and cold water pumps, (the consideration of which we have not hitherto been able to submit to mathematical treatment, because our physical data have been insufficient), from the parts devoted to the transmission of the force, as the cylinder, the beam, valves, condenser, injection-water in single action engines,

(1) Phil. Mag. [3] XXXIII, 24.
(2) Compt. Rend. XXVI, 265; Instit. 1848, 69.
(3) Phil. Mag. [3] XXXI, 73.
(4) Instit. 1848, 175.
(5) Berl. Acad. Ber. 1847, März.

Theory of machinery. Of steam engines.

which raise water from various depths, the governor, and condenser. The true theory of the latter parts had indeed been given in outline by Pambour; but there still remained much to be done in the details. Crelle promises some researches on the theory of the fly-wheel, expansion-valve, condenser, injection-water, of Watt's parallel motion, and, generally, on the most advantageous form of engine. Meanwhile Crelle give us his results relative to the fly-wheel.

In the continuation of his inquiry, Crelle(1) discusses specially the shutting off (expansion), and the question whether the water jet, which is employed, where the engine has to lift water from variable depths, or, generally, to overcome variable resistances, should not be replaced by a more certain adjustment. He answers this question in the affirmative, and proposes a simple and improved arrangement. —Crelle finds, theoretically, that Woolf's expansion-engine with two cylinders, does the greatest amount of duty, viz., four-times as much as a low-pressure condensing-engine, without expansion-valve.—Farther, he finds that much power is lost in locomotives, by the steam jet, and that another form of blast may be employed more profitably.

To this we have to add the description of some

Apparatus. For uniform circular Motion by Weight.—In practical mechanics, and in numerous physical experiments, the problem occurs—to produce a uniform circular motion by means of a weight. Jacobi(2) finds the method hitherto employed—that of connecting the barrel on which the weight acts, by a train of several wheels, with a spindle, which is provided with vanes, and revolves with great rapidity —inconvenient: the inconvenience arises from its complexity, and because a considerable time elapses before the motion reaches a maximum, and therefore uniform velocity, as well as because, if it be suddenly stopped, the quantity and velocity of the matter in motion causes a powerful reaction. Jacobi proposes to make the vanes revolve, not in air, but in some more resisting medium, especially in oil. At the bottom of the vessel, which contains the liquid, there is a cup in which works the end of a vertical spindle, which carries the vanes. The velocity can be regulated by immersing the vanes to a greater or less depth in the liquid, and where variable resistances occur, the adjustment can be effected by the apparatus itself by means of a contrivance similar to the governor of a steam engine.

(1) Berl. Acad. Berl. 1848, Apr.; Instit. 1848, 369.
(2) Petersb. Acad. Bull. VI. 104; Pogg. Ann. LXXI, 390.

Hydrometer-pipette.

Hydrometer-pipette.—Schafhäutl(1) proposes an instrument, which may serve to take up equal weights of liquids, whose specific gravity varies within certain limits, as, for instance, of the various sorts of beer,—by a simple method, on the principle of the pipette (beer-taster). The entire instrument is about $0^{m}\cdot4$ in length, and consists of a glass-tube of about 5^{mm} diameter in bore, which must be constructed at its upper part, in such a manner that the sectional area of the glass is equal to that of the space which it encloses. Towards the lower end the tube is blown into a spheroidal vessel, whilst at the upper is attached a closed glass bulb, which enables the whole to float as an hydrometer. The dimensions are so proportioned that the instrument holds exactly 1000 grains of water, when in the position in which the glass body displaces that quantity of water, and, by reason of the above-mentioned peculiarity of the neck, the same weight of denser liquids, into which the instrument sinks to a less depth, is enclosed, when it is placed in them. It admits of accurate use, from the level to which it first sinks down, to that of the float-bulb: indicating specific gravities from 1·000 to 1·026. For the details of the construction and adjustment of the instrument we refer to the paper.

Aneroid barometer.—The aneroid barometer, invented by Vidi(2) consists of a metal box ¼ inch deep, which has been exhausted of air and then hermetically sealed. Its upper side is thin, and its pliability is increased by concentric circles engraved upon it, so that it takes a different position with every alteration in the atmospheric pressure. The box is enclosed in a round case, and with the centre of the moveable plate is connected a train of levers, which multiplies every movement of the plate 600 or 700 times, and transfers it to an index, which traverses a graduated dial on the outside of the box. The instrument having been once compared with the mercurial barometer, it will supply the place of the latter for observation, wherever an accuracy greater than to ¼ line is not desired(3). Changes of temperature have no considerable influence on the action of this barometer. It is very portable, the case being only about 4 inches in diameter, and 1¾ in thickness.

We have still to mention papers on the following subjects: On a spherometer, by Perreaux(4); On an improved construc-

(1) Dingl. Pol. J. CIX, 209.
(2) Compt. Rend. XXIV, 975; Pharm. J. Trans. VII, 479.
(3) Pogg. Ann. LXXIII, 620.
(4) Compt. Rend. XXVII, 585.

Anercid barometer. tion of Wheatstone's chronoscope, by Hipp(1); On the measurement of periodical motions of great velocity, by Doppler, communicated by Bolzano(2); On a clock with conical pendulum, by L. Foucault(3); Observations on this instrument, by Arago(4), Winnerl(5), St. Preuve(6), and Garnier(7); On a centrifugal pendulum, with actual isochronism, by Pecquer(8); On a method of withdrawing astronomical pendulums from the influence of temperature and pressure, by Faye(9); On the compensation of astronomical clocks, by Porro(10), and by Languier(11); On an improved construction of Huyghen's parabolic pendulum, by St. Preuve(12); On a new system of hydraulic motors, by de Caligny(13) and Bourdon(14); On a screw-pump, by Guillemot(15); On a barometer, by Lefranc(16); On improvements of aerostats, by Gaudin(17); On anemometers, by Henry (18) and by Cockburn(19); On a reflecting anemometer, by Aimé(20); On the screw, as air-motor, by Planzanet(21); On a locomotive, worked by carbonic acid, by Jagu(22); On a hydraulic telegraph, by Pigoni(23).

ACOUSTICS.

Velocity of Sound in Fluid Bodies.—An apparatus has been constructed by Wertheim(24) for the deduction of the velocity of sound in fluids, from the tones which they produce in an organ-pipe. It consists of a receiver for the liquid, an organ-pipe, a pump, an air

(1) Pogg. Ann. LXXIV, 589.
(2) Pogg. Ann. LXXII, 530.
(3) Compt. Rend. XXV, 154.
(4) Compt. Rend. XXV, 160.
(5) Compt. Rend. XXV, 214.
(6) Compt. Rend. XXV, 215.
(7) Compt. Rend. XXV, 215.
(8) Compt. Rend. XXV, 251.
(9) Compt. Rend. XXV, 375.
(10) Compt. Rend. XXV, 940.
(11) Compt. Rend. XXV, 415 and 941.
(12) Compt. Rend. XXV, 392.
(13) Compt. Rend. XXVII, 420, Instit. 1848, 31.
(14) Instit. 1848, 87.
(15) Compt. Rend. XXVII, 447.
(16) Pogg. Ann. LXXIV, 462.
(17) Compt. Rend. XXIV, 306.
(18) Compt. Rend. XXIV, 877.
(19) Instit. 1848, 52.
(20) Ann. Ch. Phys. [3] XVII, 498; Ann. LXX, 578.
(21) Compt. Rend. XXIV, 446.
(22) Compt. Rend. XXVI, 339, 390.
(23) Compt. Rend. XXIV, 387.
(24) Ann. Ch. Phys. [3] XXIII, 434 Compt. Rend. XXIV, 656; XXVII, 150; Pogg. Ann. Ergänzungs. Bd. II, 497.

Velocity of sound in fluid bodies

receiver, and a manometer. The pipe may, by means of the pump, be filled at pleasure with air or with the liquid in question. Particular care is requisite in the latter case to avoid the false hissing tones, the mouth-piece of the pipe must be rather narrower and shorter than when used to blow the pipe with air, the slit must be larger, and the lip more inclined towards the inner part of the tube. Small bubbles of air, or a light powder suspended in the fluid, totally prevent the production of the tone. If all these influencing causes be avoided, the fundamental note and the harmonic upper notes are obtained according to the pressure applied. When organ pipes are blown with air, they always give a deeper tone than might be expected from the length of the pipe, and the known velocity of sound in air.—Liskovius(1) has proved, that the lowering of the tone, under circumstances otherwise similar, increases with the size of the section of the tube; the cause of this is a prolongation of the vibrating column of air beyond the end of the pipe; it is, therefore, more considerable in open pipes than in closed ones, as in the latter a disturbance of this description can only take place at the mouthpiece. If a mouthpiece is connected with two open tubes, L_1 and L_2, which give fundamental notes of n_1 and n_2 vibrations, from which the velocities of sound v_1 and v_2 may be calculated without farther correction, and if the correction x and y at the mouthpiece and upper end be expressed in the same unit as the length of the pipe, then $x + y = \frac{v_2 - v_1}{n_1 - n_2}$; and if n_1' and n_2', v_1' and v_2' have the same meaning for the covered pipes, $x = \frac{v_1' - v_2'}{2(n_1' - n_2')}$. The corrections may thus be calculated separately; one principal difficulty, however, remains, the fundamental note not being perfectly constant, but slightly varying with the strength of the current of air. If the harmonic upper notes are to be employed, the fundamental note derived is higher, proportionally to the height of the harmonic note employed.—Wertheim calculated the corrections from such notes only as were produced by equal pressures. He found, at the same time, on comparing the pressures most adapted to produce the different upper tones, that these pressures, the note being produced by either air or fluids, stand in the ratios of the squares of the terms of the harmonical progression.—Numerous determinations of the velocity of sound made in this manner never differ more than

(1) Pogg. Ann. LVII, 95; LX, 482.

Velocity of sound in fluid bodies.

one per cent. from that found by another method ($332^m \cdot 3$). The velocity of sound is, therefore, the same in the unbounded mass, as in a cylindrical column of air.

The resulting velocity of sound obtained by the measurement of notes from water, vibrating in a pipe is $1173^m \cdot 4$ at 15^0 C. Assuming the law deduced above (page 97) for solid bodies to hold good likewise with fluids, the velocity of sound thereby obtained is $= 1173 \cdot 4 \,.\, \sqrt{\tfrac{3}{2}} = 1437^m \cdot 1$, while, by observation at 9^0 C, the number $1435^m \cdot$ was found. We have to assume, therefore, that in liquids likewise, the velocity of sound in unlimited masses, stands to that in a fluid column, as $\sqrt{\tfrac{3}{2}} : 1$, which is possible only if the law of equality of pressure on all sides, no longer exists in the vibrating fluid.—By experimental determination of the corrections to be applied to the length of the pipe, by measurement of the number of vibrations, and with consideration of the proposition expressed above, the following values were obtained:

Fluid.	Temp.	Density.	Velocity of sound: in a column.	Velocity of sound: in unlimited mass.	Compressibility.
Seine-water	15^0	0·9996	1173^m ·4	1437^m ·1	0·0000491
Artificial sea-water	20^0	1·0264	1187 ·0	1453 ·8	0·0000467
Solution of Na Cl	18^0	1·1920	1275 ·0	1561 ·6	0·0000349
" " NaO, SO_3	20^0	1·1089	1245 ·2	1525 ·1	0·0000393
" " NaO, CO_2	$22^0 \cdot 2$	1·1828	1301 ·8	1594 ·4	0·0000337
" " NaO, NO_5	$20^0 \cdot 9$	1·2066	1363 ·5	1669 ·9	0·0000301
" " Ca Cl	$22^0 \cdot 5$	1·4322	1616 ·3	1979 ·6	0·0000181
Absolute alcohol	23^0	0·7960	947 ·0	1159 ·8	0·0000947
Oil of turpentine	24^0	0·8622	989 ·8	1212 ·3	0·0000800
Ether	0^0	0·7529	946 ·3	1159 ·0	0·0001002

Velocity of Propagation of Sound in Air.—Challis(1) has subjected to a new investigation, the mathematical theory of the velocity of the propagation of sound, and of the vibrations of air; he has thus given rise to a discussion in which Airy(2) and Stokes(3) have taken part, but which has as yet led to no results of great importance.

Blake(4) also, like Challis, has attacked Laplace's correction of Newton's formula for the velocity of sound. H being the height of a column of air of the same density, as at the point

(1) Phil. Mag. [3] XXXII, 276, 494; XXXIII, 98, 360, 462.
(2) Phil. Mag. [3] XXXII, 339.
(3) Phil. Mag. [3] XXXIII, 349.
(4) Sill. Am. J. [2] V. 372.

from which the sound is propagated, and of a pressure equal to that of the atmosphere, h being the height of a column of air of equal density, the pressure of which corresponds to the increased density, as actually occurring in the wave of sound, then Blake finds the velocity of sound equal to that which a body falling through the space $\frac{H + h}{2}$ acquires, while Newton had found the space of descent to be $\frac{H}{2}$, independent, therefore, of the intensity of the sound.—Blake calculates, according to his formula, the magnitude of the wave, corresponding to the velocity of 1142 feet, and the increased density of the air in the same, according to the formulæ $h = \frac{V^2}{32} - H$; $d = \frac{V^2}{32 H}$, in which the density of the surrounding air is taken as unit; thus he finds $h = 12937$ feet, $d = 1{\cdot}465$, while H is $= 27818$, a result, the fallacy of which becomes at once apparent, if we consider how small the amplitude of vibration in sounding bodies generally is, in proportion to the wave-length.—Blake is of opinion, that the dependence of the velocity of sound on the intensity, as pointed out by him, will account for the considerable discrepancies obtained in the various measurements. A more accurate consideration of the methods shows, however, that the sources of error hitherto recognized, particularly the influence of wind, suffice for the explanation of those discrepancies. Velocity of propagation of sound in air.

Vibrations of Rods and Strings.—A. Seebeck(1) has indicated a general method of calculating the position in vibrating rods, fixed at one end, of the vibrating nodes, and of the points of greatest vibration and of flexure, which, until now, had been calculated only for a rod free at both ends. The results of calculation are synoptically arranged in a table.—The second portion of the treatise, discusses the vibration of stretched rods, under which head, strictly speaking, stretched strings also belong. N. Savart and Duhamel endeavoured, the former experimentally, the latter theoretically, to prove the proposition, that if n be the number of vibrations of the string stretched, n_0 that of the string not stretched, and n_1 that of the string loosely stretched, $n^2 = n_0^2 + n_1^2$. Seebeck

(1) Pogg. Ann. LXXIII, 442.

Vibrations of rods and strings.

deduces, from the general equation of motion for strings, the following sufficiently accurate approximative formula for the i^{th} note:

$$n = i\,n_1 (1 + i^2 \delta)$$

$$n_1 = \frac{\pi}{l}\sqrt{\left\{\frac{Pg}{p}\left(1 + 4\sqrt{\frac{a}{Pl^2}} + 12\frac{a}{Pl^2}\right)\right\}} \text{ and } \delta = \tfrac{1}{2}\pi^2\frac{a}{Pl^2}$$

in which P denotes the tension, l the length, p the weight of the length-unit of the string, and a the constant of elasticity. The deviation of the i^{th} note from perfect harmony is, according to this, equal to $\frac{1 + i^2\delta}{1 + \delta}$

Bellani(1) adduces observations of Gattoni, according to which, iron wires tightly stretched in free air, sound only during a change of weather; no sound is obtained either in fine, rainy or very windy weather.

Theory of Musical Notes.—Robert Lefebvre(2) has communicated to the French Academy a mathematical theory of musical notes, combined with a discussion of the general principle of music.

Notes obtained by the electric Current.—Wertheim, in a former memoir(3) had endeavoured to prove—1stly. That the electric current gives rise to a transitory diminution of the coefficient of elasticity in conductors; 2ndly. That the conversion of iron into a magnet is likewise attended with a slight decrease of the coefficient of elasticity, which only partially disappears, with the interruption of the current.—In a second investigation(4) he endeavours to ascertain more accurately the mechanical effect exerted upon rods of iron or of steel, either by an outer current, which passes through a spiral surrounding them, or by an inner current; he farther discusses the laws of notes, produced by longitudinal or transversal concussion. Wertheim expresses the results of his researches in the following propositions: 1stly. A current passing through a helix, wound round a mass of iron, exerts an attractive influence on this mass, similar to the attraction of iron filings by the electrical conducting wire, as discovered by Arago. 2ndly. This attractive power, which is proportionate to the force of the current and the size of the mass of iron, may be considered as consisting of a longi-

(1) From Giornale dell' Instit. Lombardo, XV, in Arch. Ph. Nat. IV, 180.
(2) Instit. 1848, 398.
(3) Ann. Ch. Phys. [3] XII, 610.
(4) Ann. Ch. Phys. [3] XXIII, 302; Compt. Rend. XXVII, 505; Instit. 1848, 142.

tudinal and a transversal component. 3rdly. The former, according to the position of the helix, tends to elongate or to shorten the iron rod. 4thly. The transversal components, whose mechanical equivalent may be easily expressed in weight, occur only in an eccentric position of the iron rod; they balance each other if the axes of the rod and the helix coalesce. 5thly. The inner current exerts a sudden impulse upon the iron conductor, and there is no difference between this effect and that of a mechanical power acting in the same direction. 6thly. These mechanical effects afford a perfect explanation of all distinct notes produced by the exterior or interior current, or by a combination of both, in a rod, a thread, a plate of steel or iron. The notes obtained by the longitudinal components are the same as the longitudinal notes produced by a blow on the end of a rod in the direction of its axis.—Wartmann(1), from a series of experiments made with glass plates, the resin and tinfoil coatings of which were charged with electricity—and with wires, plates, and rods of iron, copper, and brass, which, when exposed to the inductive action of the current or of a magnet, retained their natural height of tone—considers himself justified in concluding that induction does not perceptibly alter the elasticity.

Notes obtained by the electric current.

According to De la Rive(2) a note is always produced in a metallic conductor, when an intermittent current is passing through it, while there is in its vicinity an electro-magnet, or a spiral wire surrounding it, through which a continuous current passes in the same direction as the one which produces the note. The same result is obtained, whether the conductor be employed as a straight wire, as a helix, a rod, or a tube.

If the sounding conductor be wound spirally, the intermittent current at once produces a note which is, however, increased by an exterior or interior helix with a constant current.—As soon as a constant, together with the intermittent current, is passed through the same conductor, the note ceases. Hence, it appears that the note is produced by molecular oscillations, which cease when the molecules attain a permanent position by a constant current. A tube of soft iron placed between both spiral wires increases the note, if both currents pass in the same direction; it decreases or destroys the note, if the currents pass in the opposite direction; it has no effect when split lengthways. A rod of soft iron in the axis of both spiral wires always strengthens the note, whilst rods of other metals in

(1) Arch. Ph. Nat. VIII, 177. (2) Arch. Ph. Nat. IX. 265.

Notes obtained by the electric current.

this position produce no effect whatever. De la Rive also obtained a note from a circular disc of brass, if the current passed from the centre to the circumference, or *vice versâ*. As mercury, and even the voltaic discharge, give notes when under the influence of electro-magnets, De la Rive puts forth the following general proposition: if an electric current passes through any solid, fluid, or gaseous conductor, a magnet, or electric currents in its vicinity will effect a certain transposition of the molecules; if the former current is intermittent, the molecules oscillate between the natural position of equilibrium and that imparted by the magnetism. The oscillations are the cause of a sound.

Physiological Acoustics.—In order to ascertain the cause of the same body communicating to our ear different tones at the same time, Duhamel(1) has made the following experiments. A caoutchouc thread connected consecutively with different points of an oscillating plate, producing simultaneously two or three notes, was conveyed to one ear, while the other was stopped up. He convinced himself that an impression of sound could arrive at the ear in this manner only, and yet all the notes were audible at the same time at all the different points. Hence Duhamel concludes, that if the oscillatory motion of one point be decomposed into several others, the ear is affected in the same manner, whether the component movements emanate simultaneously from several neighbouring points, or from one point only.

Scott Russel(2) has observed that if a locomotive moves with the rapidity of from fifty to sixty miles an hour, the note of the whistle heard by a stationary observer is decidedly higher or lower, as it approaches or recedes, than when heard by a person on the engine. Russell explains this phenomenon quite correctly by the composition of the velocity of the sound-waves, and that of the source of sound, the arguments of Brewster, who assumes a purely physiological cause, are, as Harris remarks, without foundation. The theory of this phenomenon had been given previously by Doppler(3), the confirmatory observations by Ballot(4) in the year 1845.—Russell considers the difference in height of the direct and reflected tones, as the cause of the painful impression made on the ear during the passage in a train under a bridge.

(1) Compt. Rend. XXVII, 457; Instit. 1848, 341; Ann. Ch. Phys. [3] XXV, 45; Arch. Phys. Nat. X, 52.

(2) Instit. 1848, 288: Arch Ph. Nat. IX, 138.

(3) On the coloured light of double stars, by Chr. Doppler; Prague 1842.

(4) Pogg. Ann. LXVI, 321.

Segond(1) has made some investigations on the origin of the different sounds of the human voice. According to his observations, the smaller the space of the windpipe, the throat, the mouth, and the nose, the clearer and shriller the voice becomes; with regard to the explanation of the nasal voice, Segond calls attention to the difference arising from the circumstance of the sound passing through the cavity of the nose, or of its resounding only in this cavity when closed. In the latter case the character of the nasal voice is most decidedly apparent. Physiological acoustics.

Segond farther has instituted researches on the human voice, on inspiration(2), and on the connection between the total movement of the glottis, and the height and strength of the note(3).

Apparatus.—A hand-organ has been described by Stein(4), and an akumeter, or instrument for measuring the acuteness of hearing, by Marloye(5), made according to Blanchet's directions.

OPTICS.

Sources of Light. Development of Light by Heat, and during Chemical Processes.—Draper has communicated researches on the production of light by heat(6) and by chemical action(7). To ascertain the temperature of incipient incandescence, Draper made use of a platinum wire of $\frac{1}{20}$ inch in thickness, which was heated by means of a voltaic current, a rheostat being employed in the circuit. The temperatures were measured by the expansion of the platinum wire. In a dark room the wire began to be incandescent at 525^0; this temperature was fixed by Newton at 335^0, by Davy at 433^0, by Wedgewood at 508^0, by Daniell at 528^0. Copper, antimony, gas-carbon, lead, and iron, become luminous at the same temperature as platinum, and it appears that the temperature of incandescence is identical in bodies of very different nature. Many minerals, how-

(1) Compt. Rend. XXV, 204; Arch gén. de Médec. Mars 1848; Jahrbücher der gesammten Medicin LXI, 9—12.
(2) Compt. Rend. XXVI, 252; Instit. 1848, 63; Jahrb. d. ges. Medic. LXI, 11.
(3) Compt. Rend. XXVII, 85; Jahrb. d. ges. Medic. LXI, 12.
(4) Compt. Rend. XXIV, 333.
(5) Compt. Rend. XXV, 676: XXVI, 580.
(6) Phil. Mag. [3] XXX, 345. (7) Phil. Mag. [3] XXXII, 100.

Sources of light. ever, especially such as contain lime, are exceptions. Draper found that limestone, marble, and particularly fluor-spar, shine at a lower temperature than iron.—Prismatic decomposition of the light emitted by the platinum-wire proved, that generally the least refrangible rays appear first, whilst the quantity of the more refrangible ones increases with the temperature. The fact that the spectrum underwent a partial elongation, in the direction of its red extremity also, Draper explains by the increased intensity of the light generally. At 654° the orange ray principally was visible, and, in the place of yellow, a tint, which may be designated as grey. It was only at 1163° that all the colours exhibited considerable brilliancy, their extent being little shorter than the daylight-spectrum. Availing himself of Bouguer's photometric method, Draper found that, with the rise of temperature, the intensity of light increased slowly at first, but afterwards with progressively increasing rapidity. At 525° it is equal to 0; at 1038° equal to 34; at 1420 equal to 1234, or 36 times greater than at 1038°.—Radiated heat, likewise, as pointed out by experiments with the thermo-multiplier, increases much more rapidly than the temperature. The quantity of radiant heat at 545° being taken as unit, the amount emitted at 800° is 2·5; at 1038°, 7·8; at 1310°, 17·8.

Draper subjected to prismatic analysis the light emitted by anthracite-coal and wood-charcoal, burning and then gradually expiring, the former in atmospheric air, the latter in oxygen gas. He found that there is a connection between the refrangibility of the light which a burning body yields, and the intensity of the chemical action going on; that moderate processes of combustion emit only the less refrangible rays of the spectrum, whilst the refrangibility increases with the increasing intensity of the chemical action. This, however, by no means justifies the conclusion of Draper, that for each degree of combustion, rays of a certain colour are developed, and that a flame, in which the activity of combustion decreases as we advance inwards, is a system of concentric shells, presenting the different colours of the spectrum in such a manner that a horizontal section of the flame would exhibit the appearance of a rainbow-ring. The brightest part of the flame in which the carbon particles are floating in a state of most powerful incandescence, emits rays of all colours, as proved by the foregoing experiments, and by those on the light evolved during ignition; the light developed in the outer shell, which is hottest, being chiefly blue, whilst in the inner shell the red predominates. The fact that coloured flames present many rays of the spectrum, but with a preponderance of certain

rays, is not new. (Radicke, Optics, II. 201.) When analyzing a horizontal zone of a spirit flame, Draper found all the coloured rays; the edge of the prism being placed horizontally, the narrowest spectrum was produced by the red, the broadest by the violet rays, which extend towards the border. The yellow part was marked by a brilliant line, Brewster's monochromatic ray. The colour of the carbonic oxide-flame, which, in atmospheric air, appears blue, is not changed in oxygen gas; the red flame of cyanogen gas, on the other hand, assumes a dazzling brilliancy, its spectrum being enlarged, especially towards the violet end.—The prismatic spectrum was essentially changed by introducing air into the interior of an oil-flame, by means of the blow-pipe; Draper mentions that then the blue point of the flame no longer gave red or orange rays, the spectrum consisting of five separate spaces, one yellow, two green, one blue, and one violet.—Draper's view that, during chemical action, the material particles enter into vibrations, which, in the case of combustion, may rise from 400 billions to 800 billions in the second, may be admitted. The regularity, however, exhibited by the differences of the wave-lengths corresponding to Frauenhofer's lines, which he found to be in the ratio of the numbers 1, 2, 4, 6, 7, 9, 10, cannot be considered as conclusive, inasmuch as Frauenhofer has by no means selected the strongest of the 2000 lines composing the spectrum, his main object being the acquisition of regular intervals. Sources of light.

Nature of the Candle-Flame.—Volger(1) has recently subjected the flame of the candle to a new analysis. After synoptically arranging the ascertained constituents and products of decomposition of the various kinds of fat during combustion, he proceeds to examine the gradual development of the flame on ignition. The so-called *flame-bud,* (Flammenknospe,) a globular blue flammule, is found to be first produced at the summit of the wick; this is the result of the combustion of carbonic oxide, hydrogen and carbon, and is surrounded by a reddish violet halo, the *veil.* The increased heat now gives rise to the actual flame, which shoots forth from the expanding bud, and is then surrounded at its inferior portion only by the latter. The interior consists of a dark gaseous cone, containing the immediate products of the decomposition of the fatty acids, and surrounded by another dark hollow cone, the *inner cap.* Here we already meet with carbon and hydrogen, which have resulted from the process of decomposition, and we distinguish this cone from the inner one, by its yielding soot. The *external cap* constitutes the most luminous

(1) Pogg. Ann. LXXII, 82.

Sources of light. portion of the flame, in which the hydrogen is consumed, and the carbon rendered incandescent. The surrounding portion is but slightly luminous, deposits no soot, and in it the carbon and hydrogen are consumed.

E. Becquerel(1) has investigated the effect produced by the various parts of the spectrum upon Canton's phosphorus and the phosphorus of Bologna, (sulphides of calcium and of barium,) and has observed, that the most refrangible rays (those beyond the violet) give rise to phosphorescence, and that spots, of more or less intense action, may be distinguished in this portion of the spectrum. He has also found that the rays intervening between the violet and red portion destroy phosphorescence, after having previously increased it for a short space of time, or after having increased the emission of all available rays. Draper(2) communicates the fact, that the above results may be found in a work of Wilson's, dated 1776.

Matteucci(3) has published a note on the phosphorescent matter in fishes, and on marine phosphorescence.

Theory of Light.—Cauchy(4) communicates the following results obtained in reference to the three rays of light, which correspond to the simple vibrations of the ether:

1. Assuming the waves to be plane, the three rays are propagated with velocities, the squares of which are the roots of a cubic equation. Two roots correspond to the rays that have hitherto been observed by physicists; they are equal as regards substances that produce simple refraction; unequal, though but with a slight difference, as to those with double refraction, and to homogeneous substances, which divert the plane of polarization; they are imaginary in metals and opaque bodies.

2. The two principles of corresponding motion, and of the continuity of the motion of the ether, give rise to the equations of condition, which suffice for the purpose of ascertaining the character of the polarization, and the intensity of the rays which are reflected or refracted at the surface of opaque or transparent media.

3. As to the third ray, calculation proves it to disappear if the undulations of the incident light are either perpendicular to the plane of incidence, or if they pass off parallel or perpendicular to the reflecting surface; and, lastly, that it is extinguished for every medium at an appreciable distance from the plane of separation.

(1) Ann. Ch. Phys. [3] XXII, 244; Compt. Rend. XXV, 632.
(2) Phil. Mag. [3] XXX, 87. (3) Ann. Ch. Phys. [3] XXIV, 358.
(4) Instit. 1848, 229 and 398.

Theory of light.

The quotient of the unit by the coefficient of extinction of the third ray, is changed in value in the transition of the ray from the first to the second medium, excepting when the surface completely polarizes the light, under a certain angle of incidence. The difference of the two values multiplied by the ratio of refraction, gives the small coefficient contained in the formulæ relating to transparent bodies, as proved by Jamin's experiments.

4. Other phenomena appear to indicate the existence of the third ray, such as the loss of light, which occurs in the reflected ray in oblique incidence, and as the polarization of dispersed light observed by Arago.

A theory of the propagation of light-rays and of polarization, has been founded by Challis(1), upon a new doctrine, regarding the constitution of the luminiferous ether, which he assumes to be compressible.

Mac Cullagh(2) has communicated an essay on a dynamic theory of the reflection and refraction by crystals.

Rectilinear Propagation of Light. Aberration of Light.—The aberration of light, which is easily explicable on the assumption of the theory of emission, is acknowledged to become a more complicated problem when viewed upon the principle of undulation, inasmuch as the rays which pass through space on approaching the earth, enter into the ether agitated by the rotation and translation; their course, under these circumstances, requiring to be demonstrated. Fresnel had cut the knot by assuming that the earth moved, with all the solid and fluid parts that pertain to it, through the tranquil ether, in the same manner as a net with wide meshes would pass through the air. Physicists have not been satisfied by this improbable assumption. The mathematical discussion of this matter, which took place especially during the year 1846(3), has been resumed in 1847 and 1848, by Powell(4), Challis(5), and Stokes(6).

Interference, with considerable Retardation. — Fizeau and Foucault(7) have constructed an apparatus for instituting observations of the most various phenomena of interference. Babinet, Arago, and Regnault, who were appointed to report on the subject to the

(1) Phil. Mag. [3] XXX, 365; Instit. 1848, 59.
(2) Trans. of the Royal Irish Acad. XXI.
(3) Doppler, Abh. der böhm, Ges. 5. F. III, 747. Stokes, Phil. Mag. [3] XXVII, 9; XXVIII, 15. 76. 335; XXIX, 6. 62. Challis, Phil. Mag. [3] XXVII, 321: XXVIII, 90. 176. 393. Powell, Phil. Mag. [3] XXIX, 425.
(4) Phil. Mag. [3] XXX, 93.
(5) Phil. Mag. [3] XXXII, 168.
(6) Phil. Mag. [3] XXXII, 343.
(7) Instit. 1848, 189.

Interference, with considerable retardation.

French Academy, have designated the invention as one of the highest importance, and calculated to facilitate the study of the simplest as well as of the most complicated optical phenomena. Rays issuing from a narrow opening and parallelized by a lens, are conducted through one, two, three, or even as many as five powerfully refracting prisms. The coloured rays are thus most completely separated, and those of the same denomination are united by a second lens into a single point. The spectrum exhibits the dark lines very perfectly defined, and may be examined upon a white screen, a ground glass surface, or, directly, by means of a micrometric lens, without an intervening medium. The inventors of the apparatus have been thus enabled to produce fringes with very great retardations, both by means of the mirrors, as well as by retardation of one ray by twofold reflection in a glass plate, or by double refraction in plates of calcareous spar of 5^{mm}, or rock-crystal of 50^{mm} in thickness. They have observed the phenomena presented by chromatic polarization, and have measured the coincident retardations, as well as the constants of rectilinear, circular, and elliptical polarization; so as to deduce numerous theoretical conclusions of importance. Their essays have been admitted into the *Recueil des savans étrangers.*

New Case of Interference.—Baden Powell(1) has investigated a new case of interference. If into a hollow prism, filled with oil of sassafras, anise, or cassia, a strip of glass be dipped, so that only those rays pass through it which enter at the broadest part of the prism, the spectrum of a beam of light is traversed by black bands, parallel to the origin of the light, and to the refracting edge of the prism. If fluids be employed which refract less than glass, for instance oil of turpentine or water, the strip of glass must be immersed into the narrower part of the prism, the broader portion being left free. If we term the indices of refraction for the strip of glass, and for the fluid, m and n; the wave-length of a ray, λ; the same magnitudes for a second ray, m', n', and λ'; the thickness of the plate, d; and the number of the bands between both coloured rays, a; we shall find $a = d \left\{ \frac{m-n}{\lambda} - \frac{m'-n}{\lambda'} \right\}$. If plates be employed which afford double refraction, two rows of bands are obtained, superimposed on each other.

Analysis of Fraunhofer's Interference-Spectrum.—Mossotti(2), as early as 1845, published at Pisa a separate essay on the characters

(1) Instit. 1848, 314; Phil. Mag. [3] XXXIII, 155.
(2) Pogg. Ann. LXXII, 509.

Analysis of Frauenhofer's interference-spectrum.

of Frauenhofer's interference-spectra, in which he communicated formulæ expressing the dependence of the wave-length and of the intensity upon the position of the coloured ray in the spectrum. The interference-spectrum must be considered as the normal, the prismatic as a distorted spectrum. If we suppóse the entire interference-spectrum to be divided into 360 parts, represented by 2π, λ expressing the wave-length, which corresponds to an arc ϕ, measured from the centre of the spectrum, we find, from observation, that

$$\lambda = 553{\cdot}5 + 184{\cdot}5\phi;$$

we thus obtain for the extremities 369 and 738, the millionth part of a millimeter being the unit. The formula

$$n = \frac{1}{\nu} = i + h\left(\frac{\lambda_0}{\lambda}\right)^2 + k\left(\frac{\lambda_0}{\lambda}\right)^4$$

expresses the index of refraction n of a ray by its wave-length λ; λ_0 being the wave-length of a certain ray, the deviation of which requires separate measurement in every instance. If more measurements be made than there are unknown quantities, the coefficients i, h, and k, may be calculated according to the method of least squares.—Let x be the angle between λ and λ_0, then

$$\frac{\sin\frac{1}{2}(\phi + \psi + x)}{\sin\frac{1}{2}\phi} = i + h\left(\frac{\lambda_0}{\lambda}\right)^2 + k\left(\frac{\lambda_0}{\lambda}\right)^4;$$

and if G represent the intensity of a point in the refraction-spectrum, the intensity of the same coloured pencil in the interference-spectrum will be $\Gamma = n\frac{dx}{d\lambda}.G$, n being a constant coefficient. The values of $\frac{1}{n}\Gamma$ for the known 7 lines are:

B.	C.	D.	E.	F.	G.	H.
9054	30851	294375	315787	145931	39316	9471

If the axis of the coordinates be carried through the middle of the interference-spectrum, *i. e.* the ray whose wave-length $\lambda = 553{\cdot}5$, we obtain, according to Mossotti, the following equation, which is intended to express the symmetrical diminution of intensity in this spectrum on either side:

$$z^4 = \frac{1}{3}\chi\left\{1 - \frac{3\chi(1-\chi)}{1+4\chi^2.e^{-\frac{3}{\chi}}}\right\}$$

hence $z = 3\pi\frac{\lambda - 553{\cdot}5}{553{\cdot}5}$, and $\chi = \frac{1-\Gamma}{\Gamma}$. The vâlues deducible from this formula, for the refraction-spectrum, agree sufficiently.

Analysis of Frauenhofer's interference-spectrum.

Magnus(1) describes an apparatus by the aid of which he is able to produce the phenomenon of diffraction in the Torricellian vacuum. Both the source of light itself and the diaphragms are in vacuo, so that, by this means, the objections are obviated of all those who assume light to be propagated through the material parts of bodies.

Reflection of Light.—Cauchy's mathematical analysis, and the experimental investigations of Jamin and Senarmont, have generalized and simplified the expressions of the laws of reflection of light. The latter are peculiarly valuable, as they present us with a series of admirable methods of observation, and because they prove that the application of double refraction and chromatic polarization, supported by simple mathematical considerations, is productive of important results, both in regard to the accurate confirmation of optical laws, and of the measurement of the necessary constants.

We shall first adduce the formulæ of Cauchy(2), which express the intensity of the light reflected from opaque, and especially from metallic bodies, frequent reference being made to them in the subsequent experimental researches. An acquaintance with the index of refraction of any homogeneous, transparent, body, is sufficient to characterize it; in opaque bodies the refracted ray is extinguished close to the surface, Cauchy, therefore, assumes a second constant for these bodies, namely the coefficient of extinction. Let ϑ and ε be chosen, so that ϑ cos. ε and ϑ sin. ε represent the coefficents of refraction and extinction for perpendicular incidence, let I^2 and I'^2 be the intensities of the light reflected at the angle i, the incident ray being polarized perpendicularly, or parallel to the plain of incidence, we then obtain

$$I^2 = \tan.\left(\phi - \frac{\pi}{4}\right);\ I'^2 = \tan.\left(\chi - \frac{\pi}{4}\right)\ (1).$$

in which

$$\cot\phi \cos(2\varepsilon - u)\left(2\,\mathrm{arc}\tan.\frac{U}{\vartheta^2 \cos i}\right)\ \cot\chi = \cos u\ \sin\left(2\,\mathrm{arc}\tan.\frac{\cos i}{U}\right)(2),$$

when u and U are given by the following equations

$$\cot(2u - \varepsilon) = \cot\varepsilon \cos\left(2\ \mathrm{arc}\ \tan.\frac{\sin i}{\vartheta}\right);\ U^2 = \frac{\sin 2\varepsilon}{\sin 2u}\cdot\vartheta^2\ (3)$$

One of the two components, into which every ray that is rectilinearly polarized, may be resolved when reflected, and of which one is perpen-

(1) Berl. Acad. Ber. 1847, 79; Pogg. Ann. LXXI, 408.
(2) Compt. Rend. XXVI, 86; Pogg. Ann. LXXIV, 543.

dicular and the other parallel to the plane of incidence, requires in reflection a retardation δ, which is obtained by the equation Reflection of light.

$$\tan. \delta = \tan. 2 \omega \sin u,$$

ω being determined by

$$\tan. \omega = \frac{U . \cos i}{\sin^2 i}.$$

For the principal incidence (the angle of greatest polarization), $\delta = \frac{\pi}{4}$, therefore $\omega = \frac{\pi}{4}$ and $U = \sin i . \tan i$; finally, $u = 2 A$, A being the azimuth of the reflected ray, when the azimuth of the incident ray is $= \frac{\pi}{4}$. Having measured i and A, and calculated u and U, they are introduced in the following equations deduced from (3)

$$\tan. (2 \varepsilon - u) = \tan. u \cos. (\pi - 2 i) ; \; \vartheta^2 = \frac{\sin 2 u}{\sin 2 \varepsilon} U,$$

and we are enabled successively to calculate ε and ϑ, ϕ and χ, and lastly the intensities I^2 and I'^2.

It is well known that, in reference to the reflection of light, transparent and metallic bodies have been considered hitherto as two distinct groups; the former were stated always to reflect with rectilinear polarization in any azimuth, a ray that had been polarized rectilinearly, it having been assumed that the difference of phase of the two systems, perpendicular and parallel to the plane of incidence, was from 0^0 incidence to the angle of polarization $= 0$, or $= 2 \pi$, from that to 90^0 incidence $= \pi$. The metals, on the other hand, were said to present, instead of complete polarization, a maximum of polarization only, and to convert the rectilinear undulation, unless perpendicular or parallel to the plane of incidence, into an elliptical one, the difference of phase gradually increasing from 0^0 incidence to the main incidence, from 0 to $\frac{3 \pi}{4}$ and from the principal incidence to 90^0 from $\frac{3 \pi}{4}$ to π.—A few transparent substances of very high refractive power, such as diamond, appeared to form links between these two groups, as, within certain limits, they presented elliptical polarization. Dale(1) has enumerated a series of non-metallic substances, possessing a high coefficient of refraction,

(1) Sill. Am. J. [2] III, 262, from Athen. Nr. 986; Inst. 1846, 368.

Reflection of light. which exhibit elliptical polarization; as indigo, artificial realgar, diamond, sulphide of zinc, antimony, glass, fused sulphur, tungsten, carbonate of lead, hyacinth, arsenious acid, garnet, idocrase, helvine, labradorite, hornblende, chromate of lead, litharge, indian ink. His opinion is that elliptical polarization is the universal law, and that, probably, no substance presents perfect polarization; he assumes that the residue of unpolarized light in substances possessing a low index of refraction may be too trifling to be observed, and thinks that the mathematical theory of reflection should comprehend under *one* equation the reflection both of metals and transparent substances with a high and low coefficient of refraction.

Jamin(1) does not appear to have been acquainted with this view of Dale's, although he assumes the doctrine to be an established truth, which he states that he has proved by a very accurate method of observation, the particulars of which, however, he does not communicate. The results he arrives at are, that the division of homogeneous media, hitherto adopted, into such as are transparent and polarize the reflected ray rectilinearly, and such as are metallic and opaque, and present elliptical polarization, should no longer be retained, the case of elliptical polarization being the general one. If reflecting substances be arranged in the sequence of their coefficients of refraction, the elliptical polarization of the reflected ray, as we gradually proceed to the less and less powerfully refracting media, diminishes more and more, until at last we arrive at the point of rectilinear polarization, to which Fresnel's theory applies. Thus, the angle of maximum polarization, scarcely perceptible in the case of silver, becomes more and more distinct, and the difference of phase of the two vibrations which are perpendicular to one another, varies from π to 2π between boundaries of which one is below, the other beyond the angle of polarization. These boundaries, which in metallic substances are coincident with the tangential and perpendicular incidences, approach one another, include in glass an angle of from 4^0 to 5^0 only, and, lastly, meet in the angle of polarization. But few bodies present the quality of polarizing light completely and in a straight line; it occurs in those whose refractive power is nearly equal to 1·4, and it is to them only that Fresnel's formulæ are strictly applicable.—On examining substances with a still lower refractive power, elliptical polarization again presents itself, with the difference, that we now find a retardation of the vibrations which

(1) Compt. Rend. XXVII, 147.

fall perpendicularly upon the plane of incidence as compared with those that lie in the plane of incidence; the reverse of what occurs in more powerfully refracting substances. Jamin terms the latter *positive*, the former *negative* substances.—On account of the slight susceptibility of the eye, the angle of polarization may, even if the polarization is not absolutely complete, be confounded with the principal incidence, of which the difference of phase $= (\frac{3\pi}{2})$ and the measurement of which is attainable with extreme accuracy. Brewster's law, according to which the tangent of the angle of polarization is equal to the ratio of refraction, may be retained numerically for the principal incidence.—The two constants of reflection of metals, namely the principal incidence and the ratio of the amplitudes of the two components belonging to the ray which is reflected in the angle of polarization, and also the azimuth of the reflected ray, must now be retained for transparent substances also, however small the value may be, which the latter constant generally assumes in this case. Jamin notices that the formulæ of Cauchy, which included, in addition to the ratio of refraction, the coefficient of ellipticity, have been retained by the author in their generality, for those substances only of which the diamond is the type; as regards other bodies, they have been limited, in accordance with the observations which have pointed out elliptical reflection as a special case only. These formulæ now reassume their universal value.

Reflection of light.

Jamin(1) gives an indication of his method when he states that he reflected polarized solar light from transparent substances, and, after conducting it through two quartz prisms of the same angle, placed crosswise, analysed it with a Nichol's prism. The dislocation of the parallel fringes invariably indicated a difference of phase existing between the rectangular components.

Metallic Reflection.—The laws of metallic reflection have been subjected to a new investigation by Jamin(2), with the aid of more accurate methods. The numerical results accord to an extent hitherto unknown in this kind of research with the formulæ of Neumann, to whom, however, Jamin does not at all allude, as well as with those obtained by Cauchy, (page 130).

For the purpose of measuring, (under different angles of incidence,) the *intensities* of the rays polarized in the azimuths 0° and 90°, Jamin made use of a flat mirror, composed half of metal and half

(1) Compt. Rend. XXVI, 383; Instit. 1848, 93; Pogg. Ann. LXXIV, 248,
(2) Ann. Ch. Phys. [3] XIX, 296; Pogg. Ann. Ergänz. Bd. II, 437.

Metallic reflection. of glass, in such a manner that the two plates joined in a straight line so as to form one plane. The polarized rays were reflected at the boundary line, and then received on a doubly refracting prism. Let β and β' be the azimuths of the principal section of the prism, for which the ordinary image of the metal equals in intensity the extraordinary one of the glass, and the ordinary one of the glass the extraordinary one of the metal, then we obtain, upon the basis of the well-known formulæ of Fresnel for the azimuth of polarization 0^0 :

$$J^2 = \tan.^2 \beta \cdot \frac{\sin^2 (i-r)}{\sin^2 (i+r)} = \cot.^2 \beta' \frac{\sin^2 (i-r)}{\sin^2 (i+r)},$$

and for the azimuth 90^0 :

$$I^2 = \tan.^2 \beta \cdot \frac{\tan.^2 (i-r)}{\tan.^2 (i+r)} = \cot.^2 \beta' \frac{\tan.^2 (i-r)}{\tan.^2 (i+r)};$$

as the light is all but extinguished on the glass plate in the vicinity of the angle of polarization, we here meet with a gap of a few degrees. As it is necessary to be acquainted with the coefficient of refraction of glass for the calculation of J^2 and I^2, Jamin determined its value by measuring the azimuth A′ of a reflected ray, coincident with the azimuth $\frac{\pi}{4}$. As $\tan. A' = \frac{\cos (i+r)}{\cos (i-r)}$, and consequently $\tan. r = \frac{\tan.\left(\frac{\pi}{4} - A'\right)}{\tan. i}$, we may employ various incidences and adopt the average value.—A Carcel lamp, the flame of which was placed in the focus of a lens, afforded the luminous source; a plate of red glass rendered the light homogeneous. Experiments made with steel plates and speculum-metal, afforded remarkably concordant results with the formulæ of Cauchy, which we have already given.

As the *difference of phase* which increases with the incidence 0^0 to 90^0, from 0 to $\frac{\lambda}{2}$, is $\frac{\lambda}{4}$ for the maximum polarization, two reflections from the same metal yield, under the principal incidence, the retardation $\frac{\lambda}{2}$, so that we recover rectilinearly polarized light; for the condition of the restitution of the rectilinear vibration is known to be, that the retardation of one of the two rectangular components is equal to $n\frac{\lambda}{2}$.—When we have three reflections from parallel mirrors, it will be necessary to select one angle of incidence larger, and one smaller than that of the principal incidence; viz. those which in *one* reflection

Metallic reflection.

yield differences of phase $\frac{\lambda}{6}$ and $\frac{\lambda}{3}$, so that after the last reflection we obtain $3 \cdot \frac{\lambda}{6} = \frac{\lambda}{2}$ and $3 \cdot \frac{\lambda}{3} = \lambda$ as the difference of phase, and, consequently, rectilinear polarization. In short, when we have m reflections, there are m — 1 incidences of the restored polarization, and it is evident that, by observing them while the number of reflections is gradually increased, we are enabled to ascertain experimentally in what manner the difference of phase changes with the incidences. Two parallel metallic plates, whose relative position could be adjusted by a screw, served as reflectors; it was ascertained at what incidence a Nichol's prism exhibited a minimum intensity, which was at the same time made more apparent by the transition of colour from dark blue to dark purple, the azimuth of the incident ray being optional.—Cauchy gives us for the calculation of the difference of phase, the term $\tan. \delta = \tan. 2\,\omega \cdot \sin u$, in which $\tan. \omega = \frac{U \cos i}{\sin^2 i}$, u and U retaining the same value they have in the preceding formulæ. Experiments made with silver, steel, and zinc, afforded results agreeing satisfactorily with calculation.

An easy calculation suffices to prove the following properties of the elliptical vibration which a polarized ray assumes, when incident under the azimuth a; they are properties which in part relate to the manner in which the elliptically polarized ray is affected by a doubly refracting prism. 1. If the principal section of a doubly refracting prism is parallel to the axis of an ellipse, one image has the greatest, the other, the least intensity; 2. The magnitude of the vibration in the direction of the axis is proportional to the square of its length; 3. Every elliptical vibration may be decomposed into two rays polarized in the direction of the two axes, of intensities proportional to the squares of the axes, and of a difference of phase $= \frac{\lambda}{4}$; 4. The two images are equal if the principal section bisects the angle of both axes. Jamin has ascertained the position of the axes by means of the last theorems, as the position of the principal section, corresponding to equal images, having been ascertained, it was merely requisite to enlarge or diminish the azimuth by 45°. The measurements, which were undertaken for incidences of 30° to 86° speculum-metal and red homogeneous light being used, agreed perfectly with the result of the calculation made by means of the formulæ, $\tan. 2\,\omega = \tan. 2\,a \cos \delta$; $\tan. a = \frac{J}{I} \tan. a$, in which a represents

Metallic reflection. the azimuth of the incident ray, and ω the azimuth of the axes of the ellipse.—Incidentally to this investigation, Jamin also determined the ratio $\frac{J^2}{I^2}$ of the intensities of the rays reflected under the principal azimuths. If both images are assumed to be equal, we obtain for the azimuth ω' the equation of condition cos δ tan. 2 ω' = — cot. 2 a; and by substituting for cotan. 2 a its value, and by assuming $\frac{J}{I} = m$,

$$2 \cot. \delta \tan. 2 \omega' = \frac{1}{m \cot a} - m \cot. a.$$

If the principal section be brought into the plane of reflection the result is:

$$\omega' = 0, \text{ and } -\frac{J}{I} = \tan. \left(\frac{\pi}{2} - a\right).$$

Hence, the principal section of the analysing prism being in the plane of reflexion, it is only necessary, for various incidences, to measure the azimuth of the incident light at which the images become equal. Experiments made with speculum-metal, with incidences of from 30° to 86°, closely agreed with the results of calculation.

The remarks made by Jamin upon multiple reflections, and particularly on the position and absolute magnitude of the azimuth of the reflected ray, the azimuth a of the incident ray being given, contain nothing that is not well known; his measurements made upon a plate of copper accord sufficiently with the results of calculation.—His observations on the reflections from mirrors inclined to one another, are also a mere recapitulation of the formulæ of Neumann and of Brewster's experiments.

Colour of Metals.—Jamin(1) has measured the two constants of metallic reflection for silver, bell-metal, steel, zinc, speculum-metal, copper, and brass, by placing, in each case, two plates, parallel to one another, upon a horizontal graduated circle, and allowing successively the various prismatic rays to fall upon them after traversing a Nichol's prism, which determined the azimuth of polarization. The azimuth, after reflection, was observed by means of a doubly refracting prism, moveable upon the circle. The incidences of restored polarization diminish for all metals from the red towards the violet, inversely as the angles of polarization for transparent

(1) Ann. Ch. Phys. [3] XXII, 311; Pogg. Ann. LXXIV, 528; Instit. 1848, 38; Compt. Rend. XXV, 714; XXVI, 83.

substances, which increase with the refrangibility of the ray. As regards silver, copper, brass, and bell-metal, the azimuths diminish from the red towards the violet; for silver, 0°·5′, for bell-metal, 7°·12′. There is a second class of metals, among which are zinc and steel, which exhibit a converse deportment. In speculum-metal the azimuths diminish from the red towards the green, and again increase towards the violet.—By means of the measured constants the intensity of the reflected rays may be easily calculated, according to the formulæ of Cauchy, which we have communicated above, and the correctness of which has been proved by numerous experiments. Colour of metals.

The following are the main results of these formulæ: 1. All well polished metals are completely white when the incident ray is merely tangent; 2. When illuminated by light, polarized in the plane of incidence, they present a peculiar, very pale light, in which white predominates; 3. When illuminated by light, polarized at right angles to the plane of incidence, they present a more vivid colour with less white; 4. Perpendicular incidence leaves the peculiar colour unchanged; the azimuth naturally has no influence. Cauchy's formulæ for the last case, J being the intensity, i the incidence of restored polarization, are:

$$J^2 = \tan. (\phi - 45);\ \cos \phi = \cos 2\ A.\ \sin 2 \left(\text{arc}\ .\ \tan. = \frac{\cos i}{\sin^2 i}\right).$$

a being the initial azimuth, and x′, x″, x‴, the azimuths of the ray that is polarized, and then rectilinearly polarized after 2, 4, 6, and more reflections, we obtain:

$$\tan. x' = \tan^2 A\ .\ \tan. a;\ \tan. x'' = \tan.^4 A\ .\ \tan. a;\ \tan. x''' = \tan.^6 A\ .\ \tan. a$$

and this affords the value of the angle A.

By this method, Jamin calculated the intensities of the principal rays after 1 and 10 reflections, and subsequently according to Newton's law of colours, (Biot's Physics, t. III. p. 445,) the colour of the metal. Let U be, according to the usual denomination, the angle which the calculated colour of each metal forms with the commencement of the red, Δ and 1 — Δ, denoting in the reflected ray the relations of this colour and of the white light; we may then form the following table:

Colour of metals.

METALS OF THE FIRST SERIES.

	After one reflection.			After ten reflections.		
	U.	Δ	$1-\Delta$	U.	Δ	$1-\Delta$
Copper .	69° 56′ Orange, very red.	0·113	0·887	43° 29′ Red.	0·812	0·188
Bell-metal.	83° 10′ Orange, yellow.	0·065	0·935	40° 40′ Red.	0·767	0·233
Brass . .	103° 13′ Yellow.	0·112	0·888	62° 50′ Orange, very red.	0·349	0·650
Silver . .	89° 0′ Orange, very yellow.	0·013	0·987	84° 32′ Orange, yellow.	0·124	0·876
METALS OF THE SECOND SERIES.						
Zinc . .	180° 67′ Blue.	0·021	0·979	264° 58′ Indigo blue.	0·188	0·812
Steel . .	74° 33′ Orange, red.	0·017	0·983	—22° 50′ Violet.	0·089	0·911
SPECULUM-METAL.						
	67° 25′ Orange, very red.	0·028	0·972	53° 59′ Red, orange.	0·292	0·708

These results are fully confirmed by experiment, if we remember that many of the colours mentioned are almost entirely concealed by strong admixtures of white. Of all the metals copper is subject to the most remarkable changes of colour when the reflections are multiplied. In a single reflection it is pale and scarcely perceptible, whereas after 10 reflections, the colour attains a remarkable lustre, and a pure purple red. This is almost homogeneous, or undecomposable by the prism. Of all the metals examined, steel is the only one which remains chiefly white, even when multiple reflections are employed.

Reflection of Light from Opaque, Metallic Crystals.—The reflection from transparent crystallized media, examined by Brewster and by Seebeck, has been theoretically established by Mac Cullagh and by Neumann. This kind of reflection is characterized by the fact, that the changes occurring round the same point are not uniform. The vibrations which are parallel and at right angles to the plane of incidence, retain their direction after reflection in a few well defined cases only; generally we find that each of these vibrations yields a parallel and perpendicular component. These components, however, invariably have phasial differences of multiples of half the circumference of the circle only; the polarization therefore remains rectilinear. The azimuth depends upon the relation of the amplitudes

of the parallel and perpendicular component in the reflected ray.—This unknown element does not, however, depend solely upon the angle of incidence, but upon the relative position of the plane of incidence to the axis of the crystal; and consequently it is altered if the reflecting surface revolve in its own plane.—When we have found two positions in which the vibrations of the reflected components remain parallel to those of the incident ray, we find that a varying ratio of amplitudes corresponds to the same angle of incidence, and *vice versa;* this ratio passes through zero for certain angles of incidence, (the angle of complete polarization.) For a perpendicular incidence the azimuth of polarization generally does not remain unchanged, as is the case in homogeneous media. On the other hand, the two amplitudes are reduced in a similar ratio, and the azimuth of polarization remains unchanged for certain oblique incidences, and for certain peculiar directions of the plane of incidence only.—To render the examination of all possible phenomena of reflection complete, the investigation of reflection from *opaque crystallized* media was still wanting; this has been supplied by Senarmont(1), by means of a very ingeniously constructed apparatus. This inquirer proceeded upon the assumption, subsequently confirmed by the investigation, that these bodies would present the peculiarities of crystalline reflection, complicated, however, by the character of metallic reflection, *i. e.* by the variable phasial difference of the two components.—His apparatus consists of a graduated circle, (placed vertically,) to which two moveable tubes of 20^{cm} in length are attached; these may be so adjusted that the zero-line of division bisects the angle of their axes. A support, moveable round a vertical axis, is fixed in such a position that the reflecting surface fixed above the axis, is placed in the centre of the divided circle and perpendicularly to it, and so that it moves in its own plane when the support revolves. A vessel may be attached in such a manner that the reflection is effected in the interior of a fluid.—The two tubes, their inferior openings being closed by parallel pieces of plate glass, vertical to their axes, dip into the fluid. The light of a Carcel-lamp is, in one tube, thrown upon a Nichol's prism, which determines the azimuth of the incident ray, and then passes through a plate, the two halves of which consist of pieces of quartz of equal thickness, cut perpendicularly to the axis of the crystal. After reflection the ray falls upon a doubly refracting prism, the azimuth of which, as well as that of the first prism, may be read off from graduated

Reflection of light from opaque, metallic crystals.

(1) Ann. Chem. Phys. [3] XX, 397; Pogg. Ann. Ergänz. Bd. II, 513.

Reflection of light from opaque, metallic crystals.

circles.—The expression for the changes effected in the light is obtained by decomposing the polarized ray $2 \sin \frac{2\pi}{T} t$ into two circular vibrations of opposite revolution, then giving one of the two systems a relative retardation δ, decomposing both of them in planes parallel and at right angles to that of incidence, assuming the diminution of the amplitudes equal to h and k, and the phasial difference to ϕ, and lastly by decomposing the vibrations of the reflected ray, in a direction perpendicular and parallel to the principal section of the analysing prism, or in other words, into the ordinary and extraordinary spectrum. The vibrations belonging to both spectra may then, if we term the azimuth of the incident ray ω, and the angle formed by the principal section of the analysing prism with the plane of incidence a, be calculated according to the formulæ:

$$O = h \sin a \cos \left(\frac{\delta}{2} + \omega\right) \sin \left(\frac{d}{2} + \phi + \frac{2\pi}{T} t\right) - k \cos a \sin \left(\frac{\delta}{2} + \omega\right) \sin \left(\frac{\delta}{2} + \frac{2\pi}{T} t\right)$$

$$E = h \cos a \cos \left(\frac{\delta}{2} + \omega\right) \sin \left(\frac{\delta}{2} + \phi + \frac{2\pi}{T} t\right) + k \sin a \sin \left(\frac{\delta}{2} + \omega\right) \sin \left(\frac{\delta}{2} + \frac{2\pi}{T} t\right);$$

now if we take $\tan. \alpha = \frac{h}{k} \tan. a$ and $\tan. \alpha' = -\frac{h}{k} \cot. a$, and reduce the values accordingly, we shall find the intensities of the ordinary and extraordinary image to be proportional, thus:

$$\left.\begin{array}{l} O_1 = (h^2 \sin^2 a + k^2 \cos^2 a) \left\{ \begin{array}{l} 1 - \cos \delta (\cos 2\alpha \cos 2\omega + \sin 2\alpha \sin 2\omega \cos \phi) \\ \quad + \sin \delta \cos 2\alpha \cos 2\omega (\tan. 2\omega - \cos \phi \tan. 2\alpha) \end{array} \right\} \\ E_1 = (h^2 \cos^2 \alpha + k^2 \sin^2 a) \left\{ \begin{array}{l} 1 - \cos \delta (\cos 2\alpha' \cos 2\omega + \sin 2\alpha' \sin 2\omega \cos \phi \\ \quad + \sin \delta \cos 2\alpha' \cos 2\omega (\tan. 2\omega - \cos \phi \tan. 2\alpha' \end{array} \right\} \end{array}\right. \quad (1)$$

The same formulæ serve to represent the intensities of O and E in quartz, with contrary revolution, if the sign of δ be changed.

These formulæ serve to demonstrate the possibility of studying qualitatively and even quantitatively all those points which are of interest in the reflexion of light, and for which the means hitherto at our disposal had not always sufficed. It may be done by observing certain conditions of the luminous field which are easily recognised, as, for instance, the isochromatic state of both segments in one image, or in both at the same time, with complementary colours, or with identical colours and complementary intensity, or finally with identical colours and equal intensity in the ordinary and extraordinary image. Such points are the retardation of one of the two components of a determined magnitude, *e. g.* of ¼ or ½ wave-length; angles of incidence for which both amplitudes are uniformly reduced, the existence of an angle of complete polarization; finally, the amount

Reflection of light from opaque, metallic crystals.

of the differences of phase, and of the term $\frac{k}{h}$ for any incidence. It must be observed, however, that in all these cases, k and h were introduced on the supposition that the vibrations, which are parallel and perpendicular to the plane of incidence, retain their directions, a case which occurs if the plane of incidence coincides with one of the principal sections of Fresnel's plane of elasticity. The two segments of quartz in that case will exhibit the same colour, provided that the above terms of intensity are independent of the sign of δ. The conditions are:

$$\tan. 2\,\omega - \cos\phi \tan. 2\,a = 0;\ \tan. 2\,\omega - \cos\phi\ .\ \tan. 2\,a' = 0 \quad (2)$$

If the same azimuth ω is to give both images uniformly, we have $\cos\phi\,(\tan. 2\,a - \tan. 2\,a') = 0$ and this condition is fulfilled if $\phi = \frac{\pi}{2}$, when $\omega = 0^0$ or $\omega = 90^0$.

If, under these conditions, we assume for the analyzer $\tan. a = 0$ or $= \infty$, the intensities are $h^2(1 - \cos\delta)$, and $k^2(1 + \cos\delta)$, or, in other words, the colours are, with the exception of their intensities, complementary. On the other hand, if we suppose $\tan. a = 1$, we have $\cos 2\,a = 2\cos a'$, and both images have the same intensity and colour.—To allow the azimuth ω to retain any value whatever when $\cos\phi = 0$, we should have $a = a' = 45^0$ or 135^0, which is an impossibility. In this case it is possible to conform to one of the equations (2) only, or if we take an azimuth at random for the incident ray, one only of the two images can be uniformly coloured. If, for instance, we assume $a = 45^0$ or 135^0, we have

$$\tan. a = \pm\frac{k}{h},$$

and the intensities,

$$O_i = \frac{2\,h^2\,k^2}{h^2 + k^2} \text{ and } E_i = \frac{h^4 + k^4}{h^2 + k^2}(1 - \cos\delta\cos a'),$$

the ordinary image becomes colourless, the other remaining coloured; the reverse occurs when $\cot a = \pm\frac{k}{h}$. The condition expressed in $\cos\phi\,(\tan. 2\,a - \tan. 2\,a') = 0$, is also fulfilled when $\tan. 2\,a = \tan. 2\,a'$, *i. e.* when $a = \frac{\pi}{2} + a'$, or when $a = \pi + a'$, which formulæ lead to the equations: $\tan. a\,.\tan. a' + 1 = 0$, and $\tan. a - \tan. a' = 0$; now, as we have generally

$$\tan. a \tan. a' + \frac{h^2}{k^2} = 0, \text{ and } \tan. a - \tan. a' = \frac{h}{k}\cdot\frac{2}{\sin 2\,a},$$

Reflection of light from opaque, metallic crystals.

the above conditions can only be fulfilled when h = k, in which case the two images are always complementary; or when h = 0, in which case we presuppose the existence of an angle of complete polarization, the intensities being $\sin^2 a\,(1-\cos\delta)$, and $\cos^2 a\,(1-\cos\delta)$, when the pictures, therefore, present the same colour and complementary intensity. — If the analyser be placed so that the ordinary image has a uniform colour, we have $\tan.\,2\,\alpha\cos\phi = \tan.\,2\,\omega$, and the two values α and $\frac{\pi}{2}+\alpha$, which satisfy this equation, yield two positions of the analyser :

$$\frac{h}{k}\tan.\,a = \tan.\,\alpha\,;\ \frac{h}{k}\tan.\,a' = \tan.\left(\frac{\pi}{2}+\alpha\right)$$

and hence we deduce :

$$\frac{h^2}{k^2} = -\cot a\cot a'\,;\ \cos\phi = \tan.\,2\,\omega\,.\frac{\sin\,(a+a')}{\sqrt{-\sin 2a\,.\,\sin 2a'}}.$$

Consequently, if we fix the azimuth of the incident ray, and measure the two conjugate azimuths a and a′ of the analyzer, which, *e. g.* render the ordinary image of uniform colour, it is possible to calculate for any incidence, the phasial difference ϕ, as well as the relation of the amplitudinal diminution. Moreover, we obtain by the formulæ (1), which have already proved so serviceable in interpreting the phenomena presented by the apparatus above described, the means of recognizing whether a change of signs has taken place in $\cos\phi$; in fact, whether ϕ has passed through 90^0 or 270^0, which may occur either by gradual progression, as is the case in metals and highly refractive or opaque metallic crystals, or suddenly (p. 140), as in homogeneous media. Let the first formula (1) be differentiated in reference to a, and ω be eliminated by means of the equation $\tan.\,2\,\omega = \cos\phi\tan.\,2\,\alpha$, and $a = \alpha = 0^0$ or $= 90^0$, which is identical with a reduction of the ordinary image to uniformity, and with placing the principal section of the analyser, parallel or perpendicular to the plane of incidence,—then we get

$$\frac{d\,O}{d\,a} = -2\,h\,k\sin\delta\,.\,\cos\phi.$$

It is necessary, according as h and k are of the same or contrary signs, or, if these magnitudes be looked upon only as absolute values, according to the denomination of $\cos\phi$, to rotate the analyser slightly to or from the stated position, if it be intended to produce the same change of colour.—By this means we are, for instance, enabled satisfactorily to determine by mere inspection, that the difference of phase between the component rectangular vibrations,

when their flection takes place from opaque homogeneous media, is 180^0, calculating from the perpendicular incidence to the angle of complete polarization, and 360^0 from this angle to the tangential incidence; $\frac{h}{k}$ at the same time assuming the value 1, 0, 1 at the three boundary points respectively, as required by Fresnel's formulæ. The angle of complete polarization may, as we previously remarked, be ascertained by means of the apparatus, by the condition, that O and E present at the same moment, the same colours for all azimuths of the analyser. Senarmont ascertained the angle of polarization to be for water = 53^0 5′, for fluor spar = 55^0 1′, for refined oil of beechnuts = 55^0 43′.—In metals, the phasial difference of the two rectangular components is 180^0, for perpendicular incidence; at the maximum polarization, it passes through 270^0, and increases to 360^0 for tangential incidence. The corresponding values of $\frac{h}{k}$ are 1, minimum, 1. Senarmont found the angle of polarization in various specimens of galena to vary from 75^0 13′ to 75^0 22′, for steel 75^0 27′, for mint-alloy 73^0 33′.—Transparent, highly refracting bodies, to a certain extent (pp. 132 and 133) form a connecting link between homogeneous transparent and metallic media, the amplitude of the vibration in the plane of incidence passing through a very small minimum value, near to which the difference of phase passes very rapidly from 180^0 through 270^0 to 360^0. The azimuth of the incident ray, or of the analyzer being zero, we find that blende, or sulphide of arsenic, present the ordinary image of a pale, though distinct green, and the extraordinary one of a vivid rose-colour; a slight revolution of the analyzer causes the former to pass into a pale and almost colourless tint, which is immediately followed by rose-colour.

Reflection of light from opaque, metallic crystals.

As regards the transparent, doubly refracting substances, which have been already very fully discussed, Senarmont has confined himself to the examination of two cases, which Seebeck appears to have neglected; he determined the oblique incidences in which the two components are reduced in equal ratios, so that the azimuth of the incident ray remains unchanged; and he also ascertained the mutation of the azimuth in perpendicular incidence. Both phenomena occur also in opaque metallic crystals; the second is even exempt from the complication which arises from elliptical polarization. — We do not obtain equal amplitudes of the component vibrations in the reflected ray for any incidence, when the plane of incidence is parallel with the principal section; it was, therefore,

Reflection of light from opaque, metallic crystals.

placed at right angles to the latter, and ω and a being assumed at 45^0, the crystal was successively immersed in air, water, and refined oil of beechnuts (n = 1·470). The values of the amplitudes are calculated according to the formulæ of Neumann (1):

Inclination of the reflected surface to the axis.	Observed incidences.	Calculated values. I.	Calculated values. J.	
45^0 23′	16^0 00′	— 0·252	+ 0·246	in air.
0 7	23^0 47′	— 0·2188	+ 0·2190	
45^0 23′	26 15	— 0·1718	+ 0·1704	in water.
0 7′	33 0	— 0·071	+ 0·1072	
	75 59	— 0·551	— 0·543	
45^0 23′	36 16	— 0·0653	+ 0·0656	in oil.
0 7	>45 0	— 0·0087	+ 0·011	
	51 7	— 0·0109	— 0·011	

In order to examine the second phenomenon, Senarmont directed light, polarized externally to the plane of incidence, in an angle differing from that of polarization, upon a thin glass plate with parallel surfaces. The reflected portion falling on an horizontal mirror, returned upon itself, so as again to impinge upon the plate of glass, passing through which it at length reached the analyzer, a doubly-reflecting prism; this contrivance strongly resembles Nörrenberg's polarizing apparatus. Let n and m be the diminutions of the amplitudes for the vibrations that are parallel and perpendicular to the plane of incidence of the glass plate, in so far as they are produced by reflection from the plate, and by fourfold refraction by this and the liquid surface; let h and k be the coefficients of the reduction suffered by the vibrations, which are parallel and at right angles to the principal section of the crystal,—we find that if the principal section coincides with the plane of incidence of the glass plate, the vibrations reach the analyzer with the amplitudes n h cos ω and m k sin ω, and if the principal section is at right angles to the plane of incidence, the amplitudes are n k cos ω and m h sin ω. If we term the azimuths of the emergent ray a and a′, we have

$$\tan. a = \frac{m\,h}{n\,h} \tan. \omega, \; \tan. a' = \frac{m\,h}{n\,k} \tan. \omega \text{ and } \frac{h^2}{k^2} = \frac{\tan. a'}{\tan. a}.$$

According to Fresnel's theory, a vibration with perpendicular inci-

(1) In the Memoirs of the Berlin Academy for 1835; Journ. de Math. de Mr. Liouville

Reflection of light from opaque, metallic crystals.

dence suffers by reflection a reduction of $\frac{l-1}{l+1}$, l representing the velocity of propagation in both media. In calcareous spar this ratio is for the vibration, perpendicular to the principal section, $\frac{m}{m+1}$, for the parallel one $\frac{\mu-1}{\mu+1}$, where $\mu = \frac{m\,m'}{\sqrt{m^2 \cos^2 \lambda + m'^2 \sin^2 \lambda}}$ so that $\frac{h}{k} = \frac{\mu-1}{\mu+1} \cdot \frac{m+1}{m-1}$. For a $= 45^0$ the result of the observation was:

Inclination of the reflecting surface to the axis.	Values of a′.	Values of $\frac{h}{k}$.		
		Observed.	Calculated.	
0⁰ 7′	31⁰ 42′	0·7859	0·7894	in air.
45⁰ 23′	38 32	0·8924	0·8902	
0 7	13 42	0·4937	0·4902	in water.
45 23	28 18	0·7329	0·7355	
0 7	0⁰ 26	0·08697	0·0752	in oil.
45 23	0 3	0·02954	0·05184	

The last observations alone differ perceptibly from the theoretical results, as the measured angles are small, and the errors of observation consequently exert too extensive an influence.

Senarmont found, that, of the opaque metallic crystals, tersulphide of antimony was the best adapted for his investigation. It crystallizes in right rhombic prisms, the plane of cleavage bisecting the angle of the optic axes, and containing the axis perpendicular to it. If the cleavage-surface be adjusted in such a manner that it may be rotated in its plane, both images simultaneously assume an uniform colour, under an incidence of $78^0\ 30'$, when the plane of incidence is parallel to the axis of the crystal, and under an incidence of $76^0\ 40'$ when perpendicular; this corresponds, in every case, to the difference of phase, $\phi = \frac{\quad}{2}$ If in either of these two positions, and under any incidence, one of the images has its halves rendered uniform, the tints of colour of the halves diverge as soon as the mirror is turned; the contrast attains a maximum when the plane of incidence has assumed an opposite position to the crystalline axis.—Whenever the ordinary image is reduced to uniformity, the two segments of E appear in colours, the contrast of which at first increases as the

Reflection of light from opaque, metallic crystals.

incidence diminishes, but, finally, again becomes less. At an angle of 18° 30′, the two images become uniform and complementary, the plane of incidence being parallel to the axis. In that case we have $\frac{h^2}{k^2} = 1$. If the incidence diminishes still farther, the images cease to be uniform at the same time, whatever may be the position of the crystalline axis. In this manner all the characters of crystalline reflection are obtained in the most perspicuous manner, and Senarmont has not neglected to add many numerical determinations(1).—The perpendicular reflection from tersulphide of antimony, presents the same peculiarities as those of calc-spar; the double refraction, however, appears to be less powerful, and we meet with a weak, but distinct dispersion of colour. — The two positions of the plane of incidence, of which we have hitherto spoken, coincide with two principal sections of Fresnel's plane of elasticity. If the axis of the crystal be inclined obliquely to the plane of incidence, neither of the two images vanishes if the double quartz prism be removed, and the principal sections of the Nichol's prism and the analyzer be placed parallel, or at right angles to, the plane of incidence; a deportment which indicates a deviation of the plane of polarization. In order to ascertain whether the ray is elliptically polarized, the reflected ray has to be analysed by means of a plate of calc-spar (placed perpendicularly to the axis) and of a tourmaline; we then observe a displacement, though slight, of the black cross and of the rings, yet only when the incident vibration is parallel to the plane of incidence, or when the incidence is not less than from 75° to 80°.—Thus we have, in opaque crystals, a combination of the characters of metallic and crystalline reflection; the fact of double refraction taking place in opaque bodies has been satisfactorily proved by the above researches, and a gap, previously existing in the experimental confirmation of the undulatory theory, has thus been very happily filled up.

Depolarization of Light.—Dove(2) remarks, that when light is thrown perpendicularly upon a rough surface, such as a white wall, it is uniformly dispersed and reflected; whereas the light thrown back by the surface of a mirror externally to the plane of incidence, *i. e.* the dispersed light is polarized in the plane in which it is observed. If a varnished oil painting is viewed with a Nichol's prism, the glare disappears. To confirm the view that natural light does not consist

(1) Ann. Ch. Phys. [3] XX, 436; Pogg. Ann. Ergänz.-Bd. II, 552.
(2) Berl. Acad. Ber. 1847, 75; Pogg. Ann. LXXI, 115; Phil. Mag. [3] XXX, 469.

of two components, polarized vertically to one another, but of vibrations perpendicular to the ray in every possible direction, Dove ground a conical aperture into a thick plate of glass, and directed sun-rays through an annular opening, perpendicularly upon the larger base of the truncated cone; at the ground lateral surface, the angle of the apex of the cone being 70° 50′, they were polarized in every possible azimuth, and intersected one another after reflection in one point. This light exhibited the same deportment with a plate of mica and with an analyzer, as natural light would do. Depolarization of light.

Newton's Rings.—Brücke(1) has attentively studied the order of colours in Newton's rings; he closely examined the colours of thin plates of gypsum in the polarizing apparatus, under a very gradual increase of thickness. In the detailed description of the colours of the six first series, he gives some corrections of the Newtonian scale.

Nobili's Rings.—Becquerel has given a good method for obtaining the coloured rings discovered by Nobili, which are formed by precipitation of metals on a metallic surface, placed as the one electrode vertically opposite to, and at a certain distance from, a metallic wire as the other. These, we are told by Becquerel, may be readily obtained in the following manner: a thin layer of a solution of protoxide of lead in potassa is poured upon a plate of German silver, the free end of a very fine platinum wire sealed according to Wollaston's method in a glass tube, being immersed in the solution, and placed in communication with the negative, whilst the disc is connected with the positive pole of a voltaic battery of from 8 to 10 elements.—Beetz(2) finds, however, that electro-gilt plates of silver or platinum are better adapted for obtaining annular systems of great regularity. As the thickness of the metallic deposit diminishes from the centre towards the margin, the rings present the inverse arrangement of the Newtonian rings; in both cases, however, the same explanation serves.

For the purpose of establishing a more accurate theory of the phenomenon, E. Becquerel represents the diminution of the thickness of the metallic layer from the centre to the circumference by the equation $y = \frac{A}{\sqrt{m^2 + x^2}}$, A being a constant, m the distance between the apex of the pole and the disc, x the distance of the point under examination from the centre of the system of rings,

(1) Pogg. Ann. LXXIV, 582.
(2) Ibid. LXXI, 71; Phil. Mag. [3] XXXIII, 7.

Nobili's rings. and y the thickness of the metallic layer; it is based upon the law of Ohm.—If m may be neglected with respect to x, the above equation is simplified,* and $y = \frac{A}{x}$; Becquerel states, that two series of observations accorded with this assumption. Du Bois Reymond(1) considers this accordance inexplicable, the equation being based upon an erroneous theory. The currents proceeding from every point of the pole expand conically towards the plate; if this circumstance be introduced in the formula by the assistance of the higher branches of mathematics, and still following the law of Ohm, we obtain the equation: $y = \frac{A}{(x^2 + m^2)\,(\sqrt{x^2 + m^2} - \rho)}$, ρ being the radius of the wire used as the pole. If we may neglect ρ and m in relation to n, we obtain $y = \frac{A}{x^3}$; so that the thicknesses of the deposit stand to one another in the inverse proportions, not of the first powers, but of the cubes of the distance from the centre. Beetz undertook to verify this equation experimentally by measuring the radii of the dark and light rings (in the second series) when under monochromatic illumination by the portions of the spectrum which correspond to the lines B, D, E and F. The concordance was extremely satisfactory, whereas with Becquerel's equation there are considerable discrepancies.—As according to the measurements of Beetz, the refracting index of binoxide of lead is 1·964, or less than that of gold, the even products of the cubes of the radii in the case of the dark rings, and the uneven products in that of the light rings, should yield nearly constant values. This, too, was sufficiently confirmed with the exception of the two external rings, which on the boundary line of the plate were necessarily presented too small, from the charge being more powerful in the centre; and this error was moreover increased by the neglect of m.

Phenomena of thin Plates in Polarized Light.—We abstain from analysing a treatise of Brewster(2), on the phenomena exhibited by thin plates in polarized light communicated in the *Phil. Mag.* of 1848; this investigation, originally published in the *Philos. Trans.* of 1841, having appeared in other journals(3) previously to the period which this report embraces, we limit ourselves to an out-

(1) Pogg. Ann. LXXI, 71; Phil. Mag. [3] XXXIII, 7.
(2) Phil. Mag. [3] XXXII, 181.
(3) Pogg. Ann. LVIII, 453, 549.

line of the chief results. If two polarized pencils of light, which are reflected from the surfaces of a thin plate lying upon a reflecting surface of another refractive power, interfere with one another, we do not lose half an undulation, or we obtain rings with a *white* centre, provided the mutual inclination of the plane of polarization be more than 90°. If this inclination be less than 90° half an undulation is lost, and rings are formed with a black centre; lastly, if the inclination be exactly 90° there is no interference of the pencils, and no rings are produced. Phenomena of thin plates in polarized light.

Theory of the Black Spot in the Centre of Newton's Rings.—G. Stokes(1) has studied the theory of the black spot in the centre of Newton's rings. His formulæ of intensity for the reflected light, prove, in addition to the results with which we are acquainted, that when the angle of incidence lies between the angle of total reflection, and another value represented by a simple term, the spot is larger in light polarized perpendicularly to the plane of incidence, than in light polarized in this plane. This result is confirmed by observation.

Iridescent Silver.—Brewster discovered, in 1829, that the iridescence observed in mother-of-pearl may be transferred to lead, tin, and fusible alloy, by a mere impression of the surface. As the appearance is transitory, on account of the oxidizable nature of these substances, Brocklesby(2) has proposed to transfer it to silver by galvanism, by introducing the fusible alloy after refrigeration into a solution of cyanide of silver as the negative pole of a small battery.

Iridescent Copper.—Dove(3), in reference to this point, communicates the fact of his having, as early as 1839, obtained galvanoplastic impressions of iridescent buttons in copper.

Iridescent Surfaces of Minerals.—Hausmann(4) has given a synopsis of all the cases in which minerals present iridescent surfaces, and has reduced the phenomenon to its various causes. The phenomenon as in blue steel, always depends upon the formation of a superficial layer heterogeneous from the rest of the mineral, and which is penetrated by the light. Such an heterogeneous layer either consists of a deposited film of another mineral, such as hydrated sesquioxide of iron, (*e. g.* upon specular iron ore), or of manganese, or depends upon a chemical alteration of the mineral

(1) Instit. 1848, 290.
(2) Sill. Am. J. [2] I, 112; Pogg. Ann. LXX, 204.
(3) Pogg. Ann. LXXI, 246.
(4) Instit. 1848, 150; Sill. Am. J. [2] VI, 254.

Iridescent surfaces of minerals.

surface, viz. an oxidation which is generally attended by an absorption of water, being associated with, or independent of the elimination of another element.

Among the minerals altered by oxidation, arsenic is distinguished by the rapid transition of the polished surface to the iridescent condition; in vacuo, however, or in dry air, it remains unchanged for many years. Bismuth, tin-white cobalt (smaltine), hard cobalt ore, arsenical iron (mispickel), bright white cobalt (cobaltine), arsenical nickel (nickeline), galena, and magnetic iron ore, belong to the same class. Among the minerals which become iridescent by oxidation, combined with the elimination of an element, we find a series of sulphides, which are converted into oxides and hydrates, such as ordinary, radiated and magnetic iron pyrites, common and purple copper pyrites (chalkosine and phillipsine). In the last mineral, the moisture of the atmosphere gives rise to the decomposition at the surface. The surfaces remain fresh, without a trace of iridescence, when exposed over sulphuric acid, under a glass bell; whereas, they become coloured in two hours if water be placed under the bell. Again, grey-antimony (stibine, tersulphide of antimony), zinkenite, feathery-antimony, dark-red silver (argyrythrose, sulphides of antimony and silver), and fahl-ore (grey-copper), also belong to this class. Oxidation, with an elimination of water, is the cause of iridescence in manganese; oxidation, with elimination of carbonic acid, in sphærosiderite (siderose); ironspar, manganese-spar, magnesocalcite (bitter-spar), and magnesite. Iridescence is caused by the elimination of hydrosulphuric acid in argyrose (sulphide of silver). In all cases in which iridescence depends upon oxidation, its production may be accelerated by raising the temperature. The changes of the surface are not always the same when occurring at high, and at the ordinary temperatures. In many minerals heat produces a vitrefaction of the superficial layer, as in lepidomelane, ilvaite (lievrite), arfvedsonite, and gadolinite.—Again, there are other minerals which merely present iridescent scales on the surface, such as ilvaite, thallite (epidote), the brown varieties of mica, and other silicates.

Metallic Lustre of Crystals.—Haidinger(1) has contributed to the doctrine of the colours in crystalline bodies, by an investigation of the metallic lustre which gives to many crystals so splendid an appearance. This lustre proves, that not only the colours of the transmitted, but also of the reflected light, are dependent upon the

(1) Pogg. Ann. LXXI, 321.

Metallic lustre of crystals.

position of the planes of crystals relatively to their axes. If we term the ordinary image of the dichroscopic lens O, and the extraordinary one E, the results of the observations are as follows. 1. Platinocyanide of potassium, in light transmitted, perpendicularly to the axis, is pale sulphur-yellow, parallel to the axis, sky-blue. In reflected light, the plane of incidence being perpendicular to the axis, O with the lustre of glass, E without lustre; the plane of incidence being parallel to the axis, O shining and colourless, E with a blue lustre; when reflected from the terminal surface, O and E equally blue. 2. Platinocyanide of barium, in transmitted light: O of a pure yellow, E yellow, with an admixture of red and green. In reflected light, the plane of incidence perpendicular to the axis: O white, E colourless and lustreless; the plane of incidence parallel to the axis: O white, and E azure-blue. If the crystal be turned to the light, in such a manner that it is illuminated by one of its terminal surfaces, the edge formed by the latter and one lateral surface, appears with a rich green lustre, which, under the dichroscopic lens, passes entirely into the image O, whereas E presents the pure yellow transition-colour. These examples will suffice to exhibit Haidinger's mode of observation. In addition to the salts which we have mentioned, he also examined platinocyanide of magnesium, which is carmine in transmitted, green, and blue in reflected light; murexide, which in transmitted light is dark-red, in reflected light, green with a gold lustre; hydrokinone, greenish-black with a greenish yellow metallic colour; oxalate of protoxide of platinum, which from an olive-green solution, is deposited with coppery red metallic lustre, and which also presents blue, brown and dark-blue colours; indigo, copper-red, gold-yellow, and brass-yellow. Haidinger(1) interprets these phenomena by assuming an additional stratum of an ether of peculiar constitution, at the boundary plane of two optic media; the first plane of which gives a reflection of white light, and from it the double refraction and dispersion of colours, are also found to proceed. A reflection of a portion of one coloured image results from the second plane: thus, for instance, it is the green colour of the extraordinary ray which is strongly reflected from the platinocyanide of magnesium. This explanation is perfectly arbitrary, as we know of no other optical phenomenon which warrants the assumption of a peculiar stratum of ether at the surface.

(1) Pogg. Ann. LXX, 574.

Simple refraction of light. New expression for the law of refraction.

Simple Refraction of Light. New Expression for the Law of Refraction.—Minding(1) has communicated an expression of Snell's law of refraction, which appears more adapted than the usual one for many purposes. Two dioptric theorems, the one by Dupin and Malus, the other, by Gergonne, are proved in a more simple manner according to Minding's new formula, than they were by their discoverers. The following is the expression of the law of refraction: There is a constant relation, viz., that of the ratio of refraction, between the cosine of the inclination of the prolonged incident ray, to a linear element, which is drawn arbitrarily from the point of incidence upon the boundary plane of the refracting medium, and the cosine of the inclination of a refracted ray to the same linear element. Assuming η and η' to be the angles formed by the prolonged incident and by the refracted ray, with the linear element lying in the plane of incidence, ϑ and ϑ' to be the angles formed by these rays with another element that is placed in the refracting plane, we obtain:

$$\sin\left(\frac{\pi}{2}-\eta\right) = n \sin\left(\frac{\pi}{2}-\eta'\right), \text{ or } \cos\eta = n\cos\eta',$$

and if δ is the angle of both elements, $\cos\vartheta = \cos\eta\cos\delta$; $\cos\vartheta' = \cos\eta'\cos\delta$, and also $\cos\vartheta = n\cos\vartheta'$, which contains the above proposition.

Ratio of Refraction of Ice.—Bravais(2) has measured the ratio of refraction of ice by the aid of Wollaston's goniometer, and has obtained the following values:

Middle of the red	1·3070	Middle of the green	1·3115
„ „ orange	1·3085	„ „ blue	1 3150
„ „ yellow	1·3095	„ „ violet	1·3170

Caustics.—Airy(3) gives us an appendix to his Treatise on the Intensity of Light in the vicinity of a caustic. De Morgan has furnished a series for computing the integral $\int_0^\infty d\,\omega\cos(\omega^3 - m\,\omega)$ whereas Airy, in order to avoid the integral $\int_0^\infty d\,\vartheta\cos\vartheta$, which he considered obscure, formerly had recourse to the method of quadratures. Both methods give concordant results.

Dispersion of Colours. Composition of the Spectrum.—Brewster(4), as is well known, several years ago proposed the

(1) Petersb. Acad. Bull. V, 113; Pogg. Ann. LXX, 268.
(2) Ann. Ch. Phys. [3] XXI, 361; Pogg. Ann. Ergänz.-Bd. II, 576.
(3) Phil. Mag. [3] XXXIII, 311.
(4) Edinb. Trans. XII, 123.

Dispersion of colours. Composition of the spectrum.

view that the spectrum consists of three fundamental colours, *red, yellow,* and *blue,* which, extending with unequal intensity over the entire length of the spectrum, thus not only produce the mixed colours, orange, green, and violet, but also distribute a quantity of white light over the spectrum, which he supposed incapable of analysis, because it consists of *different coloured rays of similar refrangibility.* This view was suggested by the character of the spectrum when examined with coloured absorptive media, as for instance, smalt-blue glass. Red is seen in this case in direct juxtaposition with vivid pure yellow, orange having disappeared, &c. Airy(1) has made an attempt to prove that the results obtained by Brewster were due to imperfect observation; he states that the modified spectrum should be compared directly with one unmodified, and that all other light should be carefully excluded; as he remembered having, some time since, instituted careful experiments with absorptive media, the results of which were at direct variance with Brewster's views. Brewster(2) has, however, completely refuted this attack, by remarking that, in his observations, all those points have been attended to, that Herschel has obtained similar results, and that an experiment, which is imperfectly related from memory, is neither qualified to upset his results, which have been obtained with hundreds of absorptive media, nor to be handed down to posterity by the historian of the inductive sciences (Whewell) as an undoubted fact.

Analysis of Sunlight.—Melloni(3) reports on Draper's investigation of the development of light by heating, and, at the same time, critically examines the experiments of Brewster, which have just been mentioned, on the constitution of the prismatic spectrum. Melloni thinks that this philosopher allowed himself to be deceived by the effect of a complex spectrum; in the homogeneous or elementary spectra, which Melloni claims to have employed in his experiments, he states that he never saw yellow in juxtaposition with red, when the orange was removed by an absorptive medium. Brewster(4) very justly and positively objects to the insinuation, as well as to the entire critiques of Draper and Melloni as altogether inappropriate.

Longitudinal Striæ in the Solar Spectrum.—If we permit the passage of sunlight through a small opening into a dark room, by means

(1) Phil. Mag. [3] XXX, 73; Pogg. Ann. LXXI, 393.
(2) Phil. Mag. [3] XXX, 153; Pogg. Ann. LXXI, 397.
(3) Phil. Mag. [3] XXXII, 262; Pogg, Ann. LXXV, 62; Arch. Ph. Nat. V, 238.
(4) Phil. Mag. [3] XXX, 461; XXXII, 489; Pogg. Ann. LXXV, 81.

Longitudinal striæ in the solar spectrum.

of an heliostat, we observe in the prismatic spectrum, especially as the opening is reduced, a greater or less number of longitudinal striæ, which Zantedeschi(1), Ragona-Scina(2), and Wartmann(3) have attributed, strangely enough, to reflection, refraction, dispersion, interference, and deflection; whilst Knoblauch and Karsten(4), Kuhn(5) and Crahay(6) proved with facility that those striæ were solely attributable to imperfections of the apparatus, roughness of the edges, particles of dust on the mirror and in the opening. The first three physicists would appear to have worked on this subject, with a view to undermining old established facts. One of them sees the longitudinal striæ better when the opening is broad; the other, when it is narrow; the three observers admit that the striæ depend upon the apparatus, and Zantedeschi, in consequence, supposes that Frauenhofer overlooked the dependence of his lines (the transverse lines) on the character of his apparatus. The theoretical discussion is obscure and unintelligible.

Theory of Natural Colours.—J. Müller, of Freiburg, is engaged in an explanation of the natural colours; he proceeds upon the assumption of Wrede(7), that colours are caused by the interference of rays reflected at the surface, and at various depths of substances. Müller(8) conducts the sunlight by means of an heliostat through a vertical fissure into a dark room, and directs it through a second fissure upon a prism of flint-glass. The spectrum is received upon a screen of transparent paper, which is graduated horizontally into inches and lines. By means of this contrivance, several of Frauenhofer's lines may be observed, and their distances compared; this apparatus also offers the advantage over examination by the telescope, of a complete survey of the spectrum. If, previously to analysis, the light passes through coloured media, broader or narrower shadows, or very numerous narrow black lines, or both phenomena, may be observed in the spectrum. The first correspond to the powerful colours of the lower order, the second to the paler colour, or the white of a higher order, the third to combinations of the lower and higher orders of colours. Similar phenomena are obtained

(1) Raccolta Fisico-Chimica Italiana, 1846, I, 373.
(2) Raccolta Fisico-Chimica Italiana, 1847, II, 483; 1848, III, 17.
(3) Arch. Ph. Nat. VII, 33; Phil. Mag. [3] XXXII, 499; Instit. 1848, 99.
(4) Pogg. Ann. LXXIV, 389.
(5) Ibid. LXXV, 455.
(6) Instit. 1848, 268.
(7) Pogg. Ann. XXXIII, 353.
(8) Ibid. LXIX, 93; LXX, 115.

by analysing interference-colours by the prism; which was effected in a very convenient manner by Müller(1), by conducting the light previous to analysis through laminæ of gypsum of various thickness. When these were inserted between two Nichol's prisms, whose planes of polarization, either parallel or perpendicular to the plane of vibration of the gypsum-plate, formed an angle of 45°, the colours of polarization were produced, the origin of which, as due to interference, has long since ceased to be a matter of doubt, and for which those coloured rays which become extinguished, may be anticipated by calculation. The purple of the second order causes a dark streak in the yellow, in the yellow of the second order the purple end of the spectrum is extinguished, the colours of the fourth order already show two dark streaks, and if successively thicker laminæ of gypsum are employed, we obtain 3, 4, 5, and finally, a great number of fine dark striæ. If three Nichol's prisms be employed, and between each pair a gypsum-plate be introduced in the proper position, we obtain combinations of two colours. If a lamina of gypsum, exhibiting the purple of the second order be combined with another which is sufficiently thick to appear white, prismatic analysis gives rise to a phenomenon, which presents some similarity to the colour of iodine-vapour. Theory of natural colours.

In order to obtain further materials for the elaboration of the theory, Müller(2) has analysed prismatically the light of 12 coloured liquids. For this purpose he placed a layer of a very concentrated liquid, contained between flat pieces of glass, before the second fissure of his apparatus (vid. supra), and then read off upon the graduated screen, the length of the colour-spaces thus extinguished; the same process was successively repeated after the addition of an equal quantity of water, &c. A solution of Paris-blue in oxalic acid (blue-ink) yielded the following results; whilst the entire spectrum extended between the divisions 44 and 70,

the concentrated solution gave light between	52	and	58
Diluted ½	50	„	60
	49	„	62
	47	„	63
1/16	46	„	64·5
1/32	45·5	„	65·5

From these results Müller has constructed curves representing synoptically the deportment of the spectrum under these circumstances. In addition to those for the liquid above-mentioned,

(1) Pogg. Ann. LXIX, 98, LXXI, 91.   (2) Pogg. Ann. LXXII, 76.

Theory of natural colours.

similar curves have been constructed for sulphate of copper and ammonia, solution of indigo, chrome-alum, tincture of litmus, mixture of bichromate of potassa with sulphate of copper and ammonia, mixture of safflower with blue ink, green ink, bichromate of potassa, solution of sesquisulphocyanide of iron in water, etherial solution of sesquisulphocyanide of iron, and carmine.—The phenomena exhibited by bichromate of potassa were very striking. A saturated solution, which was so pale that no very considerable absorption was to be expected, completely extinguished all the light from green to purple, whilst yellow, orange, and red passed through undiminished. When a concentrated solution was employed, the light extended from 63 to 69 of the scale, when diluted to $\frac{1}{16}$, only from 61 to 70; and it was not until a dilution to $\frac{1}{32}$ had taken place, that a faint glimmer appeared; even when the dilution was carried to $\frac{1}{256}$, the purple end of the spectrum was still invisible. We have still to look for a theory by which to account for these phenomena.

Brücke(1) has observed that a cuneiform lamina of gypsum, introduced between parallel Nichol's prisms, presents at its thinnest part a gradual transition from white to brown; and that lavender grey is the complementary colour of this brown when the Nichol's prisms cross one another. He has published this observation under the heading, "on the Nature of the Colour Brown."

Durocher(2), Martins(3), and Collomb(4) have communicated remarks upon the colour of glaciers, and of the water issuing from them.

Dispersion of Light in the Interior of Solid and Fluid Bodies.—J. Herschel attributed, to a superficial dispersion, the colour presented by some varieties of fluor-spar, and by solution of sulphate of quinine under reflected light, and which is different from the colour produced by transmitted light. He termed this phenomenon epipolism. Brewster(5) now shows that if intense pencils of light be employed, the phenomenon is clearly proved to depend upon dispersion taking place at a considerable depth in the interior of the substance—and that it may be observed in a large class of substances, such as various greenish kinds of glass, numerous solutions of vegetal substances, *e. g.* the colouring matter of laurel-leaves, orcine-resin, black tea, the seeds of *colchicum autumnale*, and sul-

(1) Pogg. Ann. LXXIV, 461; Phil. Mag. [3] XXXIII, 281.
(2) Ann. Ch. Phys. [3] XXI, 488; Compt. Rend. XXIV, 677;
(3) Ann. Ch. Phys. [3] XXII, 496; Compt. Rend. XXIV, 545.
(4) Compt. Rend. XXIV, 1093.
(5) Phil. Mag. [3] XXXII, 401; Pogg. Ann. LXXIII, 531.

phate of strychnine. The dispersion of the entering pencil attains its limit when all the dispersible rays have been eliminated, and in sulphate of quinine this is the case at a trifling depth, hence the remarkable epipolism of this substance. The dispersed pencil of light is polarized principally in the plane of reflection. The solution of Prussian blue exhibits distinctly the change of colour accompanying the change of the azimuth in which the ray is examined. It is blueish at 90°, carnation-red at 100°, greenish at 120°, blueish at 150°, carnation at 170°.

Dispersion of light in the interior of solid and fluid bodies.

Pleochroism of the Amethyst.—Haidinger(1) has added to his observations on the pleochroism of crystals(2), an analysis of the colours shown by the amethyst. A lamina, polished perpendicularly to the axis by Soleil, when examined with a dichroscopic lens perpendicularly to the polished surfaces, exhibited the same colours in the ordinary and extraordinary image in the centre of the plane only, whereas this property is found throughout in other uniaxial crystals. The field consisted of three blue wedges of 90°, alternating with three red wedges of 30°, in each of which the intensity of the colour increased towards the middle of the angle.—In order to obtain the greatest contrast of the colours in the two images of the lens, it is necessary to look through the crystal perpendicularly to a plane P, which is parallel to the rhombohedric planes of the amethyst, or to a surface M, which is perpendicular to the former, and parallel to the axis, or, lastly, to a surface T, at right angles to either of the preceding ones. The plane P yields in the ordinary ray a dark purple-blue, in the extraordinary ray a pure rose colour; the plane T presents the same purple-blue and a pure blue; light and dark streaks parallel to the plane P, alternate with one another; the plane M shows purple-blue, without the lens, and this colour may be decomposed under the lens into reddish and blueish purple. The chromatic phenomena just mentioned, as well as numerous others which Haidinger obtained by varying his experiments, correspond with the description which Brewster gave a considerable time ago(3) of the chromatic tints exhibited by the amethyst. They differ both from the phenomena of dichroism observed in crystals with a single optic axis, as well as from those of the trichroism of crystals with two axes. Of the following remark of Haidinger we require an explanation. He says: "Thus we find the plane perpendicular to the axis, which invariably yields two unicoloured images in

(1) Pogg. Ann. LXX, 531.
(2) Pogg. Ann. LXV, 1.
(3) Phil. Trans. 1819, p. 11.

Pleochroism of the amethyst.

all uniaxial crystals, to be dichromatic in this case; so as to correspond with the two pairs of circular vibrations undulating in contrary directions, and with unequal rapidity." It is desirable that he should have accounted more fully for the manner, in which the chromatic uniformity of the two images in the middle of the plate, as well as the laminated constitution of the amethyst, that was inferred from the striation of the plane T, *i. e.* the occurrence of laminæ, rotating to the right and left, parallel to the planes P, and parallel to three planes of a trilateral prism closing in the axis, may be reconciled with the above statement.

Double Refraction.—Brewster(1) has ascertained, that the optical deportment of those layers in the topaz which adjoin certain small cavities, indicates that the tension of gases within these cavities, caused a condensation of the constituents of the topaz whilst fluid.

Optical Character of Ammonia-Alum.—Jamin(2) informs us, that Biot discovered the octohedron of ammonia-alum to consist of eight pyramids, the apices of which occupy the centre of the octohedron, and which split parallel with the octohedral surfaces, *i. e.* the bases of the pyramids. Every pyramid forms a positive uniaxial crystal, whose crystalline axis is perpendicular to the plane of cleavage, and whose power of double refraction varies in different parts, being on an average 200 times weaker than in gypsum.—If the pyramids are united into one natural alum-crystal, the optical effects neutralize each other. If we give to a plate two parallel surfaces at right angles to one edge of the alum, we obtain the same optical effect as that produced in the compensator of Babinet.

Rotation of the Plane of Polarization connected with the Form of Crystals.—The labours of Biot(3) have established, beyond any doubt, that the rotation of the plane of polarization of a light-ray during its passage through a given substance, is caused by a power which is inherent in the molecules, and not the result of their peculiar aggregation. He considers quartz alone to form an exception, opal, hyalite, tabascheer(4), and amorphous silicic acid(5) presenting no more circular polarization than according to Herschel(6), do the silicates generally. Biot's experiments have, however, rendered it probable, that the cause of the disappearance of

(1) Phil. Mag. [3] XXXI, 101.
(2) Instit. 1848, 400.
(3) Ann. Ch. Phys. [2] IX. 372; X, 63; [3] X, 5, 175, 307, 385; XI, 82.
(4) Pogg. Ann. XIII, 522.
(5) Ibid. XXI, 289.
(6) Herschel's Treatise on Light, § 1046.

circular polarization is to be found in the transposition of the molecules, which is connected with the transition into the amorphous condition; for the specific rotatory power of a lamina of sugar that is melted, and subsequently cooled, increases in proportion as the amorphous passes into the crystalline form. No circular polarization is observed in crystals of sugar, camphor and tartaric acid, because this phenomenon is masked by the double refraction; but this does not warrant the conclusion(1), that these substances possess no power of producing circular polarization in the solid form. Circular polarization ought to be as observable in suitable crystals of sugar and tartaric acid, in the direction of their optic axes, as it is in the direction of the optic axis of rock crystal.—It seems that the substances which rotate the plane of polarization, exhibit an hemihedrous or hemimorphous formation in the crystalline condition. This is the case with sugar and tartaric acid; quartz also must be viewed as a combination of two hemihedrisms, and the tetartohedric plagihedron-surfaces indicate the direction of rotation of the plane of polarization.—According to Pasteur's(2) investigations, the two symmetrical hemihedrisms, which are obtained from a solution of racemate of soda and ammonia(3), rotate the plane of polarization in opposite directions, and this character is even preserved in the soda-salt, and in the acid which has been separated by sulphuric acid from the baryta-salt, whilst the mother liquor of the above-mentioned double salt remains indifferent to light in all stages of crystallization.

Rotation of the plane of polarization connected with the form of crystals.

Haidinger's Colour-Pencils.—Haidinger's pencils of colour have been satisfactorily accounted for by Silbermann(4), who proved that the transparent cornea and the crystalline lens are doubly refracting media, capable of yielding the ordinary colours of chromatic polarization; that the striated fibrous structure of the lens presents an analyzer similar to the fibrous agate, with this difference only, that in the former the fibres radiate from the axis in all directions. In the centre of the lens is a neutral spot, which does not polarize the light, and therefore remains colourless; the axis of the yellow pencils is parallel to the plane of polarization, which is given by a Nichol's prism held up to the eye, or by tourmaline, &c.; and to which, on the other hand, the complementary purple rays are per-

(1) Herschel's Treatise on Light, § 1046.
(2) Ann. Ch. Phys. [3] XXIV, 442; Instit. 1848, 157; Compt. Rend. XXVI, 335; XXVII, 367 and 401.
(3) Vide supra, p. 23.
(4) Compt. Rend. XXIII, 629; XXIV, 114; Pogg. Ann. LXX, 393, 401.

Haidinger's colour pencils.

pendicular. Pappenheim states, that the fibrous structure of the vitreous humour also acts in a similar manner.—This explanation renders the fact intelligible, that all eyes are not equally capable of seeing Haidinger's pencils, and why the pencils may disappear after having been observed attentively for a few moments, and again become distinctly visible upon rotating the prism suddenly through 90°.

Botzenhart(1) has observed, that if a lamina of a quartz-crystal cut perpendicularly to its axis, be inserted, Haidinger's pencils are rotated to the right or the left, according to the quality of the quartz; and that in addition to the yellow and purple pencils red and green ones are noticed, resulting from the unequal rotation of the planes of polarization of the various coloured rays.

Jamin(2), on the contrary, adopting Moigno's fundamental notion, explains the luminous pencils of Haidinger in the following manner:—If a polarized pencil of light fall upon a column of oblique glass plates, the intensity of the refracted ray varies with the azimuth of polarization; it attains a maximum if the planes of incidence and polarization are perpendicular to one another. A system of convex and concave lenses, having their axes conincident, presents to a luminous pencil, polarized in the direction of this axis, every possible azimuth of the plane of refraction. There will be two dark pencils which expand towards the circumference, in the plane of polarization, and two luminous ones perpendicular to it, and it is thus that Haidinger's pencils are produced in the lenticular system of the eye. As the various ratios of refraction cause the intensities of the various refracted coloured rays to be unequal, the pencils must appear coloured. The same variations of colour are said to be obtained by calculation as by experiment.

Experiments with the Rotating Polarizing Apparatus.—Dove(3) has adapted wheels to his polarizing apparatus, by means of which one or both the Nichol's prisms, as well as the plates that were introduced between them, could be rotated in the same or in opposite directions, and with equal or unequal rapidity, round the axis of the apparatus. He has thus obtained a means of contributing numerous interesting experiments to optics(4). When the polarizing Nichol's prism is made to rotate, the light which is rectilinearly polarized, presents the deportment of natural light; the comple-

(1) Pogg. Ann. LXX, 399; Compt. Rend. XXIV, 43.
(2) Compt. Rend. XXVI, 197; Instit. 1848, 53; Pogg. Ann. LXXIV, 145.
(3) Pogg. Ann. XXXV, 569.
(4) Berl. Acad. Ber. 1847, 70; Pogg. Ann. LXXI, 97; Phil. Mag. [3] XXX, 465

mentary annular systems which appear in the two principal positions, and the colours of thin crystalline plates mutually compensate one another so as to form white. However, the existence of polarization may be observed if the electric spark be employed as the source of light.—If the increase and diminution of the rotatory velocity during a single rotation be uniform, all the phenomena of partially polarized light present themselves, and the plane of polarization coincides with the direction of the minimum of velocity.—If both Nichol's prisms be rotated with the same velocity in opposite directions, the annular system becomes apparent, which is exhibited when both are placed opposite to one another in a state of quiescence with an azimuth of 45°. The annular system, with the white cross, appears four times in every revolution, and coincides with the points 0°, 90°, 180°, 270°, the system with the black cross appears at the 45°, 135°, 225°, 315°; consequently the impression received, is that of both phenomena covering one another. If the velocities of rotation of the two Nichol's prisms differ, the phenomenon itself rotates. When both Nichol's prisms are rotated uniformly in the same direction, the same phenomena present themselves as in light polarized and analysed circularly. These examples may suffice to characterise the experiments which Dove has multiplied by the most varied combinations of movement.—We give the following as one of the experiments which Dove instituted for the purpose of obtaining *white* by a superposition of complementary colours. He places a doubly-refracting crystal before two vertical fissures, so that the two centre-images exactly cover one another. The phenomenon, coloured by a lamina of gypsum, is then examined by means of a Nichol's prism. The two extreme images yield complementary colours, the middle one is white, owing to the superposition.—The caleidophone, when lit up at the same time with a lamp and daylight, produces curves which are objectively orange and subjectively blue; their points of intersection are said by Dove not to be perfectly white. — By employing three glasses respectively of a blueish-green, a yellow and a purple colour, Dove obtained a colourless combination; day-light appeared grey, lamp-light, on the contrary, which has a different spectrum, dingy green.

Experiments with the rotating polarizing apparatus.

Cauchy(1) has communicated some remarks on the differential equations for chromatic polarization.

Optics of the Atmosphere. Luminous Meteors. — There are several essays on luminous meteors in the periodical edited by Grunert: contributions to Meteorological Optics, Part I, first and

(1) Compt. Rend. XXV, 331.

Optics of the atmosphere. Luminous meteors.

second number: on the rainbow, by Grunert, on the three principal phenomena of halos and mock-suns by Kuhse; on twilight and the calculation of the observations of twilight of Lambert, by Grunert.

A treatise has been published by Bravais(1) on the optical phenomena which are produced by clouds containing ice.

Dispersion of Light in the Atmosphere.—Clausius(2) has made an attempt to represent in formulæ the amount of light which the atmosphere conveys to the earth, and the apparent intensity of illumination of the various points of the sky; Lambert (*"Photometria"*) and Bouguer (*" Optice"*) have been previously engaged in a similar pursuit; however, the physical data necessary to solve the question satisfactorily are still wanted. The atmosphere is supposed to be of the same density throughout, and bounded by horizontal planes; a ray of light, which enters with the intensity 1, arrives at a depth x of the atmosphere with an intensity $e^{-\delta x}$, and, consequently, at the earth's surface with $e^{-\delta h \sec \gamma}$, γ being the zenith-distance of the sun, h the reduced height of the atmosphere. If $\gamma = 0$, the intensity of the sun's light will be e^{-a}. This had been stated by Bouguer at 0·8123, by Lambert at 0·59; Clausius finally has assumed the number 0·75, and consequently, a = 0·2876819.—Atmospheric absorption is not considered, and reflection and dispersion are calculated as if caused, not by the atmospheric particles, but by the vesicles of vapour floating in the air. — Let L designate the quantity of light reaching the earth, either directly from the sun, or after any number of reflections; then a portion A . L will be returned, and is again subject to reflection in the atmosphere. ·According to Lambert, A is assumed $= \frac{1}{12}$; from the formulæ which result from the assumptions just enumerated, the following values may be calculated:

Zenith dist. of sun.	Quantity of direct sunlight.	Quantity of sun-light reduced by atmosphere.	Entire quantity of light received from the air by the earth.	Entire quantity of light reaching the earth.
5°	1	0·75	0·18599	0·93599
50°	0·64279	0·41087	0·15599	0·56686
80°	0·1736	0·03313	0·06736	0·10049

The formulæ are only applicable for zenith-distances of the sun

(1) Compt. Rend. XXIV, 962.

(2) Pogg. Ann. LXXII, 294, from Crelle's Journal der reinen und angewandten Mathem. XXXIV and XXXVI; Berlin. Acad. Ber. 1847, 200.

up to 80°. The following results, for the luminous state of the sky, may be cited as examples, that of the sun beyond the atmosphere being assumed at 1000000:

Dispersion of light in the atmosphere.

Zenith dist. of sun.	Luminosity of sun.	Luminosity of sky.								
		In the zenith.	In immediate vicinity of sun.	In horizontal circle of 60″ from zenith.			At the horizon.		
				Horizontal distance.					
				0°	90°	180°	0°	90°	180°
0°	750000	6·825	6·825	3·475	3·475	3·475	5·051	5·051	5·051
60°	562500	1·719	10·227	10·227	2·278	1·773	10·367	4·039	3·555
80°	190800	0·880	10·413	4·347	1·389	1·216	5·925	2·306	2·220

Brewster,(1) in a treatise on the state of polarization of the atmosphere, fixes the position of the neutral points; 1. Arago's neutral point lies 18°·5 above the opposite pole of the sun when at the horizon, but approaches this pole as near as 11° to 12° when the sun rises; 2. Babinet's neutral point lies 18°·5 above the sun when the latter is at the horizon, but coincides with the sun when he is in the zenith.—The polarization between each of these two neutral points and the sun, or his opposite pole, is negative, *i. e.* perpendicular to the plane of incidence, but positive between the neutral points themselves, *i. e.* in the plane of incidence. Brewster concluded that the causes which produce these neutral points, should also produce a third one below the sun, and he at last succeeded in discovering it under peculiarly favourable circumstances at a distance of 15° to 16° from the sun; this, however, is variable. When the sun occupies the zenith, the upper and lower neutral points coincide with him; they separate again as the sun sets.—Under particular circumstances, Brewster has observed that the first two neutral points are accompanied by secondary neutral points at a trifling distance.—Brewster has also examined the condition of polarization of the sky with a polarimeter constructed for that express purpose; the polarization was always neutralized with a certain number of thin plates of glass, by establishing the necessary incidences, or when the incidence was constant, by the use of the due number of plates. The point of maximum polarization is at a distance of from 88° to 92° from the sun, in the plane that passes through the sun and the zenith; the components in the plane of polarization, and in one perpendicular to it, bear a ratio of 1 : 2.—Brewster gives for

(1) Phil. Mag. [3] XXXI, 414.

Dispersion of light in the atmosphere.

the lines of equal polarization, the equation $R = 33^0{\cdot}5$ (sin D . sin D′) — 6^0 34′ (sin Z sin A); R being the degree of polarization, D and D′ the distances from the first two neutral points, Z the zenith-distance, and A the azimuth of the principal plane. — Finally, we are informed by Brewster that Zantedeschi published a treatise on atmospheric polarization in the *Raccolta Fisico-chimica Italiana* for 1846.

Optical Apparatus. Rotating Coloured Disc.—Grüel (1) has placed the rotating disc, which is employed for the purpose of showing the immeasurably short duration of the electric spark, in a vertical position, and has provided it with clock-work, by means of which the velocity of rotation may be regulated at pleasure; he has used this apparatus for the exhibition of the subjective chromatic phenomena, which have been described by Dove (2); it is also adapted to work with Newton's chromatic disc, with the stroboscopic discs, and with Opelt's siren. Dove has, on this occasion, succeeded, with the assistance of coloured glasses, in obtaining *white* by means of dioptric colours.

Application of Polarized light to the Microscope.—Brewster(3) has discovered that the application of polarized light is an excellent means of distinctly seeing under the microscope, such objects which possess double refraction, a class to which almost all crystals, as well as the majority of animal and vegetal fibres, belong. Diffraction, which causes the indistinctness of the microscopic images, disappears in polarized light, because no rays pass by at the edges of the fibres. In those cases, in which it is requisite to examine objects in a fluid without a covering-glass, or enclosed in other solid bodies with an irregular surface, polarized light almost entirely removes the injurious influence of irregular refraction by the surface. —Brewster, on this occasion, corrects an error of Chevallier's, and proves that it was not Wollaston, but himself, who removed the injurious effect of diffraction by a peculiar system of illumination for non-polarizing bodies.

We have yet to add the following optical apparatus and methods: A system of illumination for the dial-plates of large clocks by Dorey,(4) An adaptation of the Argand lamp to optical experiments, by Soleil(5); A photometer and contributions to the art of polishing glasses and metallic mirrors by Doppler (communicated

(1) Pogg. Ann. LXXV, 524.
(2) Pogg. Ann. LXXV, 526.
(3) Phil. Mag. [3] XXXII, 161.
(4) Compt. Rend. XXV. 557.
(5) Idem. XXIV, 300.

by Bolzano)(1), and by Heineken(2); A simpler form of the heliostat by Grüel(3); Alloys for mirrors and improvements of catoptrical intruments, and an apparatus for measuring the smallest deflection of a ray of light, by Doppler(4); An essay on the manufacture of the magic mirrors of the Chinese, by Stan. Julien(5); and An experiment made with one of these mirrors, by Person(6); An apparatus for illuminating microscopic objects with oblique light, by Nachet(7); Observations on the same, by Oberhäuser(8) and Chevallier(9); A proposition to illuminate the micrometer-wires by platinum-wires heated by galvanism, by Arago(10), carried out by Forment; An optical telemeter, an instrument for measuring distances, and a proposition to construct a giant microscope, by Doppler(11); A stephanoscope, by Dove(12); An improvement in the optical saccharimeter, by Soleil(13); Apparatus for saccharimetry, with a description of the method, by Clerget(14); An apparatus for measuring the rotation of the plane of polarization by fluids, under different temperatures, by Barthelemy Bianchi(15); and A doubly-refracting eye-piece-micrometer, by Arago(16).

Application of polarized light to the microscope.

Physiological Optics. Structure and Optical Properties of the Eye.—In one of his lectures at the Royal Ophthalmic Hospital, London, Bowman(17) has given a description of the structure and physical properties of the crystalline lens.

Valée(18) states, that he has found by a comparison of Krauss's measurements of the dimensions of the eye, that the exterior convex surfaces have exactly that geometrical form (curved surface of the fourth order)(19), which produces foci free from deviations; he calls them *optoidal* surfaces, and also finds that the posterior convex surfaces are, at least, so far optoidal, as the pencils of light penetrating into the eye impinge upon them.—In a subsequent

(1) Pogg. Ann. LXXII, 530.
(2) Phil. Mag. [3] XXXIII, 480.
(3) Pogg. Ann. LXXII, 422.
(4) Ibid. LXXII, 530.
(5) Pogg. Ann. XXIV, 999.
(6) Ibid. XXIV, 1110.
(7) Ibid. XXIV, 976.
(8) Ibid. XXIV, 1052.
(9) Compt. Rend. XXIV, 1097.
(10) Ibid. XXIV, 321; Pogg. Ann. LXXI, 96.
(11) Pogg. Ann. LXII, 530.
(12) Berlin Acad. Ber. 1847, 76; Pogg. Ann. LXXI, 115.
(13) Compt. Rend. XXIV, 973, XXVI, 162; Instit. 1848, 45 and 55.
(14) Instit. 1848, 61.
(15) Compt. Rend. XXV, 324.
(16) Compt. Rend. XXIV, 400; Pogg. Ann. LXXI, 405.
(17) Lond. Med. Gaz. Aug. 1848, 320.
(18) Compt. Rend. XXIV, 676.
(19) Herschel's Treatise on Light.

Physiological optics. Structure and optical properties of the eye.

memoir, Valée(1) applies to the eye the proposition, that of a series of refracting surfaces of any form, which are penetrated by rays issuing from one point, one may always be so selected, that all the rays are again concentrated into one focus. He is of opinion, that the cornea always receives, through the muscles of the eye, the form requisite for the production of sharply defined images on the retina. These changes of form might be smaller, the less the form of the other refracting surfaces differs from that of the optoidal surface.—Faye has reported to the French Academy on Valée's two memoirs(2).

Dispersion of the human Eye.—Mathiessen(3) has made the following determinations respecting the dispersion of the human eye; 1. the distance of distinct vision, with red light, from the line B, is, with far-sighted persons, more than double that with blue light from the line G. For normal eyes, the difference is less, and still smaller for short-sighted persons; 2. a white point of light, situated before a normal eye at distinct visual distance, has its focus B, $16^{mm}\cdot3$, its focus E, $16^{mm}\cdot0$, and G $15^{mm}\cdot7$ behind the centre of the eye; 3. the dispersion of the human eye is greater than that of crown-glass and of water, it approaches that of flint-glass; 4. the ratios of refraction of the crystalline lens for the lines B, E, G, are respectively 1·3634, 1·370, 1·3765.

Mathiessen is of opinion, that the means for effecting the achromatism of optical impressions, are arranged by nature externally to the real optical apparatus of the eye; an opinion which is contradicted by Valée(4). He substitutes the hypothesis, that the strongly converging pencils of light emergent from the crystalline lens are brought to a point (*appareil acuteur*) by the vitreous humour, which he considers as composed of layers of different density, and that the rays of different colours are thus contracted into one line.

Pappenheim(5) has measured the ratios of refraction of the vitreous humour in the anterior and posterior layer. He has found the former to be 1·3339 and 1·3343, the latter 1·3371, differences which are, at all events, too slight to justify Valée's *appareil acuteur*.

Brown Sequard(6) communicates some comparative observations on the action of light on the iris in the five classes of vertebrate animals.

(1) Compt. Rend. XXV, 501. (2) Compt. Rend. 843.
(3) Ibid. XXIV, 875; Pogg. Ann. LXXI, 578; Arch. Ph. Nat. V, 221.
(4) Compt. Rend. XXIV, 1096. (6) Compt. Rend. XXV, 482, 508, 510.
(5) Ibid. XXV, 901.

Defects of Vision.—Hamilton(1) gives an account of a peculiar defect of vision. A man twenty-five years of age was short-sighted, and partially blind at night. He was able to recognize horizontal lines tolerably well, but could scarcely distinguish vertical ones, and was much less able to delineate them. An experiment made with a card pierced with two holes, through which the head of a pin was observed, showed that the latter was seen by the left eye, at a distance of 6 inches or 9 inches, according to whether the holes were taken horizontally or vertically; with the right eye the ratio of 5½ to 6½ was observed. The defect was remedied by a cylindrical lens. Defects of vision.

Muscæ Volitantes.—Brewster(2) has founded on experiments with his own eye, a view respecting the *muscæ volitantes,* which differs from the explanations given by De la Hire, Porterfield, and Mackenzie. He points out as the cause, portions of the cells in which the vitreous humour is enclosed, of which the torn filaments float about in the chamber, and throw shadow and deflected light on the retina. By means of two bright light-sources placed before the eye, two shadows of the same fibre were obtained, with the aid of which Brewster has measured the apparent diameter of the *muscæ volitantes,* as well as the distance from the retina of the bodies producing it. By means of screens with appropriate openings, or lenses of different focal lengths, the divergence of the light-pencils employed may be arbitrarily placed both within or without the eye, when, by partially obscuring the lenses, the fine *muscæ* also will become visible, while in full light only the larger ones are perceptible. According to Brewster, the *muscæ* occur in every healthy eye, becoming dangerous only by too great an accumulation; they are by no means a symptom of approaching blindness from cataract or amaurosis.

Caron du Villars(3) communicates some remarks on the casual coloration of the vitreous humour.

Theory of Vision.—The magnitude of the angle which the axes of vision, directed to one point, form with each other, bears a constant ratio to the distance of the object, and it is conceivable, that from the magnitude of this angle, a direct inference respecting the distance may be drawn, without any farther aid being required by the sense of vision. This view is supported by the apparent diminution or increase of the distance of objects observed, if the intersection of the optical axes be intentionally

(1) Froriep's Notizen [3] VII, 219. (2) Phil. Mag. [3] XXXII, 1.
(3) Compt. Rend. XXIV, 1097.

Theory of vision.

placed either before or behind the objects; this Brewster(1) has confirmed by a series of new experiments. If we place ourselves in front of a large surface, *e. g.* a vertical wall, on which there is a constant repetition of the same figure at regular intervals, as, for instance, the flowers in the design of a paper-hanging, and the axes of vision be so directed, that the two nearest figures be made to coalesce, all the other pairs will likewise coalesce; the image of the wall will appear to occupy the intersection of the optic axes, whether this be situated before the wall, close to the eye, or behind the wall. The latter result can, however, only be attained, if the figures occur in a transparent surface, for instance, a plate of glass; the seat of a cane-bottomed chair placed vertically, is likewise stated to be very applicable to the latter purpose. The farther we imagine the trellis-work removed backwards, the larger the canes and the spaces are made to appear by an illusion of the imagination.

If the two sides (of equal length) of an angle be drawn on a horizontal surface, and the axes of vision be so directed that their terminal points are made to coalesce, the two lines will appear to form one, which seems shortened or lengthened, according to the intersection of the visual axes and the position of the eye with regard to the horizontal plane. The well-known experiment of holding before the eye a compass, the legs of which appear to reach to a great distance (described in Smith's Optics II, 388), is only a particular case of the above.

From all this Brewster(2) concludes that the perception of distance is included in the process of vision itself, and that the sense of sight does not require the aid of experience for this purpose; as both children and young animals, directly after birth, judge of distances in their correct proportions. This is contradicted by Whewell, who adduces the opposite experience of oculists, according to which blind people who have been operated on, required some practice before they were enabled to judge correctly of the distance of objects.

In another place(3) Brewster expresses the opinion that difference of colour has some influence in judging of distance. He states that when red and blue objects, drawn on the same surface, are contemplated, the red objects appear to be nearer than the blue ones. Hence, difference in colour would appear to be a source of optical illusion.

(1) Phil. Mag. [3] XXX, 305. (2) Instit. 1848, 371.
(3) Instit. 1848, 290.

Theory of vision.

Heineken(1) relates, with reference to the experience of Prevost and Babbage, on double vision with one eye, that he had, during two hours, seen *threefold* with his left eye, after having it closed for some time, while using his right eye aided by a lens, to divide a yard into 400 parts.

Foramen Centrale.—Brewster(2) describes an experiment which he explains by the *foramen centrale* of the retina discovered by Sömmering. If, after short repose, the eye is directed upon a sheet of paper uniformly illumined, a circular spot, surrounded by an uniform white border, is observed. Its apparent diameter is 35′, giving for the *foramen centrale* a real diameter of $\frac{1}{30}$ of an inch.

Subjective Colours. Coloured Rings, on looking through coloured Fluids.—Haidinger (3) communicates an observation of Löwe, according to which, on looking through a layer of the so-called dichromatic media, as sesquichloride of chromium or cobalt-glass, a ring is observed of the size of the iris, differing in colour from the fluid, while the space surrounded by it, of the size of the pupil, has the natural colour. It seems as if, by the particular affection of this part of the retina, the circular surrounding portion is made susceptible of the complementary impression, so that this colour appears when likewise contained in the dichromatic medium. Thus, on looking at sesquichloride of chromium, a green spot, surrounded by a violet ring, is observed. If the monochromatic ammoniacal oxide of copper be employed, the colour of the surrounding ring is only of a rather deeper blue.

Subjective Colours on the Rotatory Disc.—If a yellow and blue sector, in the ratio of 1 : 4 be painted on a rotatory disc for obtaining the intermediate green, and a small dark rod of the thickness of a thin black-lead pencil be moved parallel with itself across the disc, the rod will, according to Dove,(4) be visible as a trellis, with alternate bars, blue and yellow. The yellow bars are the broadest, they therefore appear when the rod is over the blue. The number of these bars corresponds to that of the revolutions, if only one sector of each colour be painted; as the bars may be easily counted, we obtain in this manner the number of revolutions in a given space of time.—The same phenomenon is observed if the rod be at rest, whilst the eye is moved to the side.—If the eye be moved rapidly to and fro before the disc painted with sectors, the combined colour will be observed to resolve itself momentarily into its components on that side to

(1) Phil. Mag. [3] XXXIII, 318.
(2) Instit. 1848, 289.
(3) Pogg. Ann. LXX, 403.
(4) Pogg. Ann. LXXI, 112; Berl. Acad. Ber. 1847, 77.

Subjective colours on the rotatory disc.

which the eye turns, while between the moving disc and the eye, there is an approach to a relative state of rest.

Optical Illusions. Apparent Motion of Blue and Red Spots on Red and Blue Grounds.—The fact has been known for some time, that if a blue field with red spots on it, or a red field with blue spots be moved to and fro, while artificially illumined, the coloured spots will appear to have an increased waving motion, as though they were loose upon the surface underneath. H. Taylor,(1) in explanation of this phenomenon, first calls attention to the fact, that when light and shade suddenly change their positions on a ball suspended before the eye, the former appears to swing to and fro. We may convince ourselves of this, by placing at the back of the ball, and a little to the right and left, two lights which are alternately covered.—When the red spots move in the blue field from right to left, the continued impression of red mixes at the right margin of each spot with the blue of the ground to form a darker red, similar to a border of shade; this at once passes over to the left margin when the motion is from left to right. Blue spots on red ground, on the contrary, receive a bright margin of light. The change of position of these shades and lights is the cause of the apparent swinging, just as in the case of the ball alternately illuminated on the right and left side, as described above.

Brewster(2) discusses the illusion to which the eye is subject on contemplating intaglios and cameos; it consists in confounding the convex with the concave, and *vice versâ*, and is particularly apparent on viewing them through an inverting microscope, or the eye-piece of a telescope. On the reversion of the image, a concavity appears in relief, even with a perfectly uniform shadowless illumination, if it be situate in an extended horizontal plane, the reversion of which cannot be noticed at the same time; if, on the contrary, it be situate in a narrow strip, the reversion of which can be perceived in the field of view, then it merely appears as a hollow. It is evident that the illusion must vanish on viewing the object with increasing obliquity, for in the case of a spherical hollow (appearing in relief) the whole of the elliptical margin of the imaginary convexity remains visible until it becomes a straight line, whilst in that of a convexity (appearing as a depression), that portion of the margin of the supposed concavity and part of the plane opposite to the observer become eclipsed—results the reverse of what would take place with real convexities and concavities. Shadows of course must tend to increase the illusion.

(1) Phil. Mag. [3] XXXIII, 345. (2) Phil. Mag. [3] XXX, 432.

Dove(1) calls attention to an optical illusion perceptible on riding in a train, when the objects outside the carriage appear diminished, whilst its interior is magnified in a remarkable manner.

Chemical effects of light.

Action of light on a mixture of chlorine and hydrogen.

Chemical Effects of Light. Action of Light on a Mixture of Chlorine and Hydrogen.—In the twelfth section of their investigations, Favre and Silbermann(2) have examined the action of solar light on a mixture of chlorine and hydrogen. Equal quantities of chlorine—the one, after having been exposed to solar radiation, the other in the dark—were absorbed by solution of potassa; it was found that 1 grm. of chlorine after exposure to light, disengaged 478·85 heat-units, while 439·70 units were evolved if the gas was not exposed. Favre and Silbermann account for the difference of 39·15 heat-units, by a modification of the molecules, which is stated to precede the combination with potassa, and to be attended with an absorption of heat. The exposed chlorine had undergone the same modification, under the influence of the solar heat. The number for the exposed chlorine 478·85, multiplied by the equivalent of chlorine, equals half the combustion-heat of hydrogen.—For the purpose of studying the influence of the different coloured rays of the spectrum on the mixture of chlorine and hydrogen, Favre and Silbermann filled fifty small glass tubes, placed in an upright position along the sides of a narrow trough, the gases being confined over salt water, whilst they were exposed to the solar spectrum. The level to which the salt-solution rose, in the various tubes, under the influence of light, rendered the chemical action of the coloured rays evident to the eye. Favre and Silbermann state that they have found the greatest action to take place in the morning at the line H, at noon at the line G, and in the evening at F.—They next intend to investigate the influence which the substance of the prism has upon these results.

Photographic Effect of the Various Coloured Rays.—The difficult discussion on the nature of the photographic action of the different coloured rays has been complicated still more in consequence of Draper's communications; indeed, if we place reliance on the experience of this observer, we cannot expect to see this question solved in Europe.—It is an acknowledged fact, that the most refrangible rays of the spectrum more especially exert an energetic chemical influence in general, and a photographic action in particular, while, as regards less refrangible rays, the results obtained are contradictory; it is not decided whether these rays have like-

(1) Pogg. Ann. LXXI, 118.
(2) Instit. 1848, 309; Compt. Rend. XXVIII, 362.

Photographic effect of the various coloured rays.

wise an independent photographic action, but to a smaller degree than that of the blue and violet colours, or whether they have only the faculty of continuing an action commenced by the latter, (Becquerel), or, finally, whether their action is directly opposite to that of the more refrangible portion of the spectrum, so as to neutralize their photographic effects, and to restore the sensibility of the substances in question to the action of light.—The experimental results, obtained by Fizeau and Foucault, induced these physicists to decide in favour of the latter view. Becquerel(1) believes, however, that their results, obtained, as they were, with the complex combinations of the chloride, iodide, and bromide of silver, might be explained by secondary chemical action, and he adduces some instances of such actions both from Herschel's and his own experience.

Draper(2) communicates results which he obtained in Virginia at different seasons of the year, on the photographic action of the various parts of the spectrum; they are not favourable to Becquerel's view. Draper not only found that the less refrangible portion of the Virginian solar spectrum prevented and retarded the action of daylight, even when permitted to act for hours, but also that a similar action was produced by certain rays beyond the violet. The latter was, however, only apparent in July, and even the protecting power of the red and orange rays disappeared, according to Draper, in September; it was found to exist with a portion of the yellow and green rays only, but returned in March to the red and orange.—If the daylight is excluded both previously and at the time, the protective power of the less refrangible rays is not perceptible; the Daguerreotype-spectrum being white along the space on which they have fallen.

The third of the views enumerated above, on the photographic action of the different rays of light, was defended still more decidedly by Claudet(3), who states as a general result, that every kind of ray is possessed of a peculiar photogenic power, which, at the same time, destroys that of every other kind of ray. According to this view, the action of the blue rays is destroyed by the red and yellow rays, and *vice versâ*. Claudet, however, applies the term "photogenic" action exclusively to that which imparts an attraction for mercurial vapour to silver plates, coated with a chloride, bromide, or iodide. Claudet's results are, in substance, as follows: he found that solar-rays, when

(1) Phil. Mag. [3] XXX, 214. (2) Phil. Mag. 87; Arch. Ph. Nat. V, 5.
(3) Athen. Nr. 1027; Sill. Am Journ. [2] IV, 409; Phil. Mag. [3] XXXII, 88, from Phil. Trans, 1847, II; Compt. Rend. XXV, 554; Ann. Ch. Phys. [3] XXII, 332.

Photographic effect of the various coloured rays.

coloured red by a dense atmospheric fog, or when passed through red, orange, or yellow glass, destroyed the action of white light on iodized silver plates, so as again to do away with the attraction for mercurial vapours which had been excited. The plates became again as susceptible of white light as before irradiation, and perfectly regular pictures were obtained, although a portion of the plate had been repeatedly changed by white, and restored by red, orange, and yellow light. Claudet anticipates two useful applications of these results; 1stly, that the plates may be prepared in open daylight, instead of in the dark, as they may be rendered susceptible before use, merely by subjection to red light; 2dly, that a picture may still be corrected if, on subjecting it to the vapour of mercury, it is found to have been too long exposed to light.—If the period of irradiation by white light be taken as the unit, red light requires a period of 50, orange light 15, yellow 10, to remove the action. These rays, however, are stated to possess in addition to the antagonist influence, likewise a peculiar photographic action, red 5000 times, yellow 100 times weaker than white; but this action must be of a nature perfectly different from that of the blue and violet rays, as it would otherwise be incapable of coming into action at all under the simultaneous opposing influence of red and yellow. Claudet concludes from all this, that the photographic action cannot consist in a reduction of the silver, with the elimination of iodine, bromine, or chlorine, as the plate did not lose its sensitiveness to light after so many actions and reactions.—Hunt(1) also communicates an experiment which is favourable to the opinion that certain rays of light protect the sensitive substances from chemical change. He directed light, previously transmitted through a yellow medium, upon highly susceptible photographic paper, simultaneously exposed to full sunlight by reflection. The white paper was blackened, with the exception of the stripe under the action of the yellow light, which remained white.

Gaudin(2), on the other hand, confirms the results obtained by Becquerel. He has succeeded in obtaining perfect pictures by the continuous power of rays which have passed through an orange-coloured glass, without the application of mercury; these Claudet(3) endeavours to explain by a crystallization of the chloride of silver, and will not admit that they belong to the class of Daguerreotype-pictures. Gaudin also states, that if chloride of iodine be employed, the orange-yellow light, not only acts continuing, but

(1) Instit. 1848, 291. (2) Compt. Rend. XXV, 639.
(3) Compt. Rend. XXV, 763; Instit. 1848, 291.

Photographic effect of the various coloured rays.

independently, whilst the rays that had passed through red glass only continue the action.

With regard to the observations of Becquerel and Gaudin, Claudet(1) states, that he also had seen cases in which the effect of red and yellow rays upon iodized silver plates had been continuing instead of destroying the action. Yet, as he had also observed the reverse as positively, he considered that it appeared to confirm Draper's results, which tended to prove that the effect of the rays is essentially modified by the season of the year. The variations in the results have, however, only occurred in silver plates that were iodized in the ordinary manner. If the iodizing process be continued until the plates have passed through the series of yellow, red, blue, and bluish-green tints, and this series be repeated, or if the more susceptible(2) bromine- and chlorine-compounds be employed, the yellow and red rays are said, by Claudet, always to destroy, and never to continue the action.—The non-appearance of the pictures, which is frequently ascribed to the imperfect preparation of the plates, or to the condition of the fluids which are to accelerate the action, is attributed by Claudet in the majority of instances to the state of the light, inasmuch as the destroying rays may increase in intensity so as to overpower the efficient rays.

Coloured Photogenic Drawings.—E. Becquerel(3) states, that if a small plate of silver be held over chlorine-water, at a distance of a few centimetres, it assumes a whitish tint after a few minutes; and if a solar spectrum, condensed into a few centimetres, be now thrown upon it, we obtain a representation of the latter with its peculiar colours. The yellow appears least distinctly. The plate may be still better prepared by immersing it into chlorine-water, until it has assumed a whitish, slightly rosy tint, or into dilute hydrochloric acid, the plate being connected with the positive pole of a galvanic battery, or, lastly, into a solution of chloride of copper.—In order to obtain the yellow colour perfectly, the plate, after being well prepared, should be placed under a shade of combined red and blue cobalt glass, when it becomes purple in diffused light. The orange, yellow, green and blue colours of the spectrum are then very readily retained. Becquerel considers the compound, formed by the above method, to be a subchloride, or a mixture of white protochloride with the

(1) Phil. Mag. [3] XXXII, 199; Ann. Ch. Phys. [3] XXII, 348; Compt. Rend. XXV, 763, 938.

(2) Phil. Mag. [3] XXXII, 215.

(3) Ann. Ch. Phys. [3] XXII, 451; J. Pr. Chem. XLIV, 358; Ding. Pol. J. CX, 25; Compt. Rend. XXVI, 181; Instit. 1848, 45, 54, 341.

subchloride, because when treated with ammonia, it becomes white, and behaves like the white chloride.—The coloured prismatic impression, however, is not retained under the influence of light; it is destroyed by the solvents of the protochloride, such as ammonia and hyposulphite of soda. Coloured photogenic drawings.

Daguerreotypes.—But few new observations have been contributed to the production of Daguerreotype-pictures.

Belfield Lefèvre and Foucault(1) state, that if a silver plate be polished and iodized in the usual manner, and then exposed to three times the quantity of bromine-vapour, which suffices to render the plate most susceptible to light, so that it assumes a dark-purple tint, the plate will be found to have acquired less susceptibility, but to be more adapted to reproduce the gradations of light of the lightest as well as of the darkest parts in the most complete detail; this is a quality, the absence of which is much felt in plates that are prepared in the ordinary manner.

Kilburn(2) remarks, that electro-silvered plates take a better polish, and are more susceptible of the influence of light than Daguerreotype-plates prepared in the ordinary manner.

Boué(3) recommends the same process.

Kilburn(4) obtained Daguerreotypes in a time of ten minutes, by the aid of the flame of a tallow candle, or an oil-lamp.

Photographic Pictures on Paper.—The methods of producing photographic drawings on paper have been improved.

Blanquart-Evrard(5) moistens the paper which he uses for large photographic drawings, by placing several moistened sheets behind it, and pressing it between two plates of glass. The fluids with which the two sides of the paper alternately are moistened, are a solution of 1 part of nitrate of silver in 30 parts of distilled water, and of 25 parts of iodide of potassium with 1 part of bromide of potassium in 560 of distilled water. After the last bath, the paper is dried and preserved in the dark; when required for use, it is again moistened on the first side with a solution of 6 parts of nitrate of silver in 11 of crystallizable acetic acid and 64 of water, and then exposed to the light in the camera obscura. The picture is brought out by the application

(1) Ann. Ch. Phys. [3] XIX, 125; Phil. Mag. [3] XXX, 213.
(2) Phil. Mag. [3] XXXII, 547; Dingl. Pol. J. CIX, 314.
(3) Compt. Rend. XXIV, 466.
(4) Phil. Mag. [3] XXX, 378.
(5) Ann. Ch. Phys. [3] XX, 100; Compt. Rend. XXIV, 117, 653; XXV, 812.

Daguerreotypes.

of a concentrated solution of gallic acid in large excess(1); it is then washed with water, a solution of 1 part of bromide of potassium in 40 of water poured over it, again washed and dried, when the negative picture is complete.—The paper for the positive pictures, a great number of which may be produced by means of the negative paper, is prepared in the usual manner, by means of solutions of chloride of sodium and nitrate of silver.

Saguez(2) gives the following method for preparing photographic paper: 1. For the negative picture. Choose very fine paper of uniform transparency; immerse for three to four minutes in a solution of 5 grm. iodide of potassium in 120 grm. water; dry for twelve hours in the air. The paper assumes a pale rose colour, and may be kept in this condition for months in a dry place. If used for the purpose of producing a picture, a small quantity of a solution of 5 grm. nitrate of silver, in 10 grm. acetic acid, and 60 grm. water, is poured on a plate of glass, and the paper laid upon it. It becomes covered with a dense and very sensitive layer of white iodide of silver (according to Saguez(2) *sous-iodure*). 2. For the positive picture. The paper is placed upon a solution of 1·25 grm. of chloride of sodium in 40 grm. of water until it is moistened uniformly; it is then pressed between blotting paper, placed upon a solution of 5 grm. of nitrate of silver in 30 grm. of water, and removed, after a time, to be dried in a dark place. No care will, however, prevent its assuming a slight rose tint. The positive picture is fixed by means of a solution of 30 grm. of hyposulphite of soda in 300 grm. of water.

Iodized Paper for Photogenic Drawings.—To prepare iodized paper for photogenic drawings, by means of a single solution, Jordan(3) recommends the precipitation of nitrate of silver by iodide of potassium, and the re-solution of the precipitate in a strong solution of iodide of potassium. This solution is to be transferred to the paper by means of a glass rod; the paper after drying is to be immersed in water, which precipitates the iodide of silver on the paper. This is now laid upon water with the iodized surface downwards, in order entirely to remove the iodide of potassium.

Brooke(4) states, that he has obtained photographic paper of extreme sensibility, by adding a small quantity of iodide of potassium to bromide of potassium.

(1) Ann. Ch. Phys. [3] XXI, 447. (2) Compt. Rend. XXV, 633.
(3) Mech. Mag. 1848, n. 1304; Dingl. Pol. J. CX, 78.
(4) Instit. 1848, 66.

Schönbein(1) states that starch-paste, when mixed with recently prepared iodide of lead, so as to give it an intense yellow colour, and exposed to the sunshine, rapidly assumes a black-blue colour, and that this mixture, in fact, is the most susceptible of all known substances of the influence of light. Iodized paper for photogenic drawings.

Transference of Daguerreotypes and Drawings to Photographic Paper.—Poitevin(2) has published a method by which Daguerreotype-pictures and engravings may be transferred to photographic paper. The Daguerreotype, before the iodide of silver is washed off with hyposulphite of soda, is to be immersed in a solution of sulphate of copper, so as to be employed as the negative pole of a voltaic battery. The copper is deposited upon the particles of mercury only, and not upon the iodide of silver, which is a bad conductor. The latter is then removed and the plate dried. If a solution of gelatine be now poured upon the plate and allowed to dry, the copper, and, consequently, a negative picture, may be removed with the gelatine; the picture is then carefully placed upon photographic paper, and exposed to diffused light for a quarter of an hour. The picture has afterwards to be washed with water and hyposulphite of soda, and to be dried. In order to obtain an impression of a drawing or an engraving, it is to be laid upon an iodized plate, and exposed to the light; the negative picture which results is then exposed to the vapour of mercury, and the subsequent process adopted is the same as that in the last case.

Method of obtaining engraved Metallic Plates from Drawings or Engravings.—Poitevin(3) has also invented a method by which we may obtain on plates raised or sunk impressions from drawings or engravings; these plates in their turn may be used for multiplying the impressions.—The engraving is exposed to iodine vapours, which only adhere to the black parts; the sheet is then attached to a silver plate, polished according to Daguerre's method, by means of slight pressure; the iodine is transferred to the silver, so that layers of iodide of silver are formed corresponding to the shadows of the engraving. The plate is then immersed into a concentrated solution of sulphate of copper, and used as the negative pole of a weak battery; it is removed before the iodized portions are coated with copper. The plate is at once washed, and the iodide removed by hyposulphite of soda; the copper surfaces are then oxidized by

(1) Pogg. LXXIII, 136.
(2) Compt. Rend. XXVII, 13; Instit. 1848, 221.
(3) Compt. Rend. XXVI, 153; Instit. 1848, 46; J. Pr. Chem. XLV, 233.

Method of obtaining engraved metallic plates from drawings or engravings.

heat until they become dark brown, the exposed silver surfaces are amalgamated after cooling, and the plate being covered with two or three layers of gold leaf, the mercury is volatilized by heat. The gold is brushed off from those parts which are covered with oxide of copper, and to which it does not adhere. The oxide of copper is then dissolved by a solution of nitrate of silver, and the silver, as well as the subjacent copper, exposed to the action of dilute nitric acid. The parts covered with gold are not affected, so that the etching may be carried to any depth; the plate which is thus obtained, may be employed for taking impressions, in the manner in which wood-cut-blocks are used.

In order to obtain plates engraved as deeply as the plates used for ordinary copperplate engravings, a plate of gilt copper is employed. By proceeding as above, the light parts are covered with copper, and the shaded parts being deprived of the iodine, the gold amalgam is removed from the shaded, and the oxide of copper from the light parts by acid. The latter will then be protected against the further action of the acid by the gold, and we obtain a deep engraving.

Peculiarities of certain Vapours adapted to the Production of Pictures.—Nièpce de St. Victor(1) has discovered two new properties of iodine vapours, and endeavoured to employ them in multiplying works of art.—The first property consists in the deposition of iodine vapours upon the lines of engravings, drawings, &c., whether they consist of printer's ink, ink not containing gum, Indian ink, or minium. If we then place the iodized sheet upon paper, a plate of glass, porcelain, or ivory, &c., which has been covered with a layer of starch, the drawing is transferred with the blue, violet, or red colour of iodinated starch. The best method is to immerse the drawing, first in ammonia-water, and then to pass it through water acidulated with sulphuric, hydrochloric, or nitric acid. After drying it is exposed to iodine vapours, and the above-mentioned operations performed; the sheet is then placed upon the plate covered with starch-paste, and, after the picture has been completely dried, a transparent varnish is applied, and it is put under glass. Several impressions may be taken without renewing the coating of iodine.—The picture may also be transferred and fixed upon silver or copper.—Iron, lead, tin, brass also receive the picture, but no means have as yet been discovered of fixing it.—The second peculiarity of iodine

(1) Ann. Ch. Phys. [3] XXII, 85; Phil. Mag. [3] XXXII, 206; Sill. Am. J. [2] VI, 258.

vapours consists in their being deposited mainly upon the prominent parts of embossed plates, so that we are also enabled to take impressions from these.—Chlorine possesses the same property as iodine; but the picture is so faint, that it has to be rendered visible upon silver plates by mercury, on copper by ammoniacal vapours. Bromine produces no effect whatever.—The product of the slow combustion of phosphorus presents the same deportment as iodine; the fumes of nitric acid are mainly deposited on the light parts, and therefore give rise to a negative picture upon silver and copper plates. With regard to embossed plates, these fumes deport themselves like iodine. A negative picture may be obtained also from engravings, by exposing them to the vapour of warmed chloride of lime. Chevreul(1) has made a lucid report on the above subject.

Peculiarities of certain vapours adapted to the production of pictures.

Photogenic Drawings on Glass.—In order to transfer photogenic drawings to glass, Nièpce(2) directs that from twelve to fifteen drops of iodide of potassium be added to the white of three eggs, which are to be beaten up to a froth, and the albumen allowed to run off. The former is put into a square vessel of porcelain, into which the glass plate is introduced vertically, and let down gently by a hook at one side, until it assumes the horizontal position and is covered by albumen, which is then dried at a temperature of not more than 15° or 20°. The plate is then introduced into a mixture of acetate and nitrate of silver, in the same manner as it was immersed into the albumen, washed in distilled water, and placed in a dark chamber. Gallic acid is employed to bring out the picture, bromide of potassium to fix it.

Porro(3) communicates an account of a picture obtained by Zantedeschi, which is analogous to those of Moser, and was produced by porcelain plates coloured with oxide of cobalt upon white porcelain surfaces placed opposite. Laurent(4) remarks, that he had previously obtained, and published an account of, similar pictures.

Seguier(5) has made a detailed report on the recent progress of photography to the society for the promotion of the Arts in Paris, incidentally to a distribution of prizes.

Photographometer.—An instrument was constructed by Jordan

(1) Compt. Rend. XXV, 785.
(2) Compt. Rend. XXVI, 637; Instit. 1848, 183; J. Pr. Chem. XLV, 230.
(3) Compt. Rend. XXV, 762. (4) Ibid. 784.
(4) From Bull. de la Soc. d'Encour. Avril, 1848, 195, in Dingl. Pol. J. CVIII, 451.

Photographometer. in 1839, and improved by Hunt, for the purpose of measuring the intensity of the chemical power of solar light. A hollow cylinder, into which a triangular opening, with one angle upwards, is cut, is made to turn on its axis, which is placed perpendicularly to the plane of the ecliptic so as to rotate with the sun. A second cylinder, covered with photographic paper, revolves within the former in the opposite direction. The rays of the sun impinge upon the points as they pass by the triangular opening; the nearer they lie to the apex, the shorter the time of exposure will be. The more the visible photographic effect approaches the apex, the more powerful may the light be assumed to be. This apparatus, as well as the instrument constructed by J. Herschel, in 1840, requires to be moved by clockwork, and both only serve to measure the intensity, which varies with the period of the day. Claudet(1) has lately succeeded in producing what he terms a photographometer, by means of which we are enabled to measure, not only the intensity of the chemical rays, but also the relative susceptibility of the plates or chemical papers which have been prepared according to different methods. The plate or paper is attached at the lower edge of an inclined plane, and covered with a metallic plate, which is perforated horizontally with a row of equi-distant round holes. A second disc slides along the inclined plane, in which there are corresponding holes of 1, 2, 4, 8, 16, 32, and 64 millimetres in diameter. This second plate is fixed in a black cloth, which moves with it, in such a manner that the rays of light can only impinge upon the prepared plate, during the time which the openings of the moving plate occupy in passing over those in the one at rest. It is evident, that the ratios of the periods of operation for the adjacent perforations must be as 1, 2, 4, 8, &c. When a very weak light is employed, as in instituting a comparison between the solar and lunar light, it is necessary to let the moveable plate fall repeatedly, and to calculate the ratios of the intensities accordingly.—If we wish to compare plates that have been prepared according to different methods, they must be placed in juxtaposition, and two moveable plates allowed to slide down at the same time, as the intensity of the light varies every minute.

Claudet has ascertained by means of his apparatus, that pure solar light renders iodo-bromide of silver susceptible of the vapour of mercury in $\frac{1}{1000}$th of a second. He considers the apparatus adapted to solve the following questions. What is the effect of the compound light, and what that of the separated rays of the

(1) Phil. Mag. [3] XXXIII, 329; Instit. 1848, 318; Compt. Rend. XXVII, 370.

solar spectrum? What is the amount of loss in the chemical rays by ordinary or total reflection, or by refraction through lenses? What is the intensity of the chemical rays in the various sources of light? What influence does the atmosphere exert upon the chemical rays? Photographometer.

Ronalds(1) has invented a method of photographic self-registration of meteorological and magnetic phenomena.

MAGNETISM.

Sustaining Power of Magnets.—It is now several years since P. W. Häcker(2), an ironmonger at Nürnberg, proposed for the sustaining power of horse-shoe steel magnets, (when so far saturated that their magnetic power can no longer be weakened by frequent removal of the armature), the purely empirical formula(I), deduced from numerous experiments,—

$$\text{(I)} \quad z = a \sqrt[\frac{3}{2}]{P},$$

where P represents the weight of the magnet, z its power, both in Bavarian loths (1 kilogr. = 1·786 Bavar. pounds = 57·152 Bavar. loths), and a a constant magnitude for a homogeneous mass of steel. With good magnets the value of a can be raised, according to Häcker to that of log. a = 1·6, and, when external disturbing influences are excluded, will remain constantly at this point. However, this value a depends much on the nature of the steel, as well on the working of it in the fire as on the degree of hardness, but not sensibly, within certain limits, on the size or form of the magnet. The weight of a great number of magnets which were examined was between $\frac{1}{120}$ loth, and 40 pounds, with very different dimensions of the legs, whose length in the heaviest magnet reached 31 inches. Within these limits it seems to be indifferent, whether the section of the limbs is round or rectangular, whether it is square or oblong, whether one of them is somewhat longer or shorter than, or nearer to or farther from, the other, indeed, even whether they consist of one piece or of several laminæ.

Thus also the sustaining power of straight magnetic rods, of weights

(1) Sill. Am. J. [2] III, 428. (2) Pogg. Ann. LVII, 321.

Sustaining power of magnets.

between $\frac{1}{4}$ and 81 loths, and of lengths between 2 and 18 Parisian inches, may be calculated, when they have been raised as nearly as possible to their point of permanent saturation, by doubling the power found to belong to one pole(1).

Häcker gives(2) for the times of oscillation of straight magnets, moving in a horizontal plane the empirical expression,—

$$T : t = \sqrt{L}\ \sqrt[3]{F} : \sqrt{l}\ \sqrt[3]{f},$$

where L and l represent the lengths, and F and f the section-surfaces of the rods. If then for the section we substitute the weight divided by the length, making the time of oscillation of a rod of length l, and weight 1 equal to c we obtain:

$$\text{(II)} \quad T = c\ \sqrt[3]{P \sqrt{L}}.$$

The experiments from which this formula is deduced, were made with magnet-rods from 3 to 22 inches in length, and from 1 to 103 loths in weight. Häcker takes log $c = 0{\cdot}432$, in this case, however, we must again express P in Bavarian loths, and L in Parisian inches(3).

The times of oscillation calculated according to this formula, within the specified limits, agree tolerably with observation, as well in the case of cylindrical as of rectangular rods; with the latter, even when they consist of several laminæ of inconsiderable breadth laid one upon the other.

In the course of these researches the remarkable observation occurred to Häcker, that with straight magnet-rods, at any degree of saturation, the product $a\,c^2$ remains always constant. If now we multiply equation (I) by the square of equation (II), we obtain—

$$\text{(III)} \quad z\,T^2 = a\,c^2\ \sqrt[3]{P^4 L};$$

an equation, by means of which $a\,c^2$ being ascertained once for all, the attractive power of a straight magnet, for all degrees of saturation, can be deduced from its time of oscillation, which can be determined very easily and accurately. Häcker determined for Nürnberg log $a\,c^2 = 2{\cdot}464$.

He also endeavoured to determine the conditions, on which depends

(1) Pogg. Ann. LXII, 366. (2) Ibid. LVII, 337. (3) Ibid. LXXII, 68.

the duration of the oscillations of magnets whose dimensions do not fall within the above-mentioned limits. Since, however, the results obtained by him in this direction do not seem to offer an equal interest either in their practical or their scientific bearings, it may suffice here to refer to the papers which treat of them(1). The fact is not unimportant, that untempered steel retains somewhat more than half the magnetic power that can be conferred permanently on tempered steel.

Sustaining power of magnets.

Häcker does not speak of the quality of the armatures selected by him, which nevertheless, as we must conclude from the later experiments of Dub on the sustaining power of electro-magnets(2), must also have a very important influence in the case of steel-magnets; and this, besides, has been before pointed out by earlier experimenters.

With reference to the sustaining power of electro-magnets, Jakobi and Lenz(3) had enounced, as founded on observation, the proposition, that, under conditions in other respects similar, the total attraction, *i. e.* the mutual adherence, of two straight cylindrical electro-magnets, or of one electro-magnet and one armature of soft iron, is proportional to the square of the strength of the current. This proposition, stamped as it seemed to be with truth, can, however, according to J. Dub's researches, be accepted as correct, only within very narrow limits, and for certain forms of armature, while for armatures of other forms, the proportions appear entirely different. Dub shows generally, by numerous experiments, with keepers of various dimensions, that these have a far greater influence on the amount of the sustaining power than has been hitherto supposed. Not only does the mass of the keeper, but also its length, and the magnitude of its surface in contact with the magnet, claim consideration as of essential import. We obtain from Dub's researches no information concerning the laws of this connection, so that it is not, therefore, as yet possible to give any general statement of the most appropriate form and magnitude of the armature.

Some experiments on the same subject have been narrated by Barral(4), according to which the attraction increases with the weight of the keeper, and reaches its maximum, when the electro-magnet and keeper are of equal weight. The series of experiments of Dub, which are far more comprehensive, and more fully

(1) Pogg. Ann. LXII, 63; LXXIV, 394.
(2) Ibid. LXXIV, 465.
(3) Pogg. Ann. XLVII, 403.
(4) Compt. Rend. XXV, 757.

Sustaining power of magnets.

described, agree with this indication only so far, that for a given electro-magnet, and given diameter of the keeper, a certain amount of sustaining power cannot be exceeded. This limit, however, seems to depend more upon the length than on the weight, and to be the more slowly attained, the greater the strength of the current.

Barral has also examined the law of the diminution of the sustaining power under increasing distance of the mutually attracting surfaces, and gives for it the expression $y = \frac{A}{B+C^x}$, where y represents the force of the attraction in kilogrammes, and x the distance in millimetres; A, B, and C being constants dependent on the force of the current, as well as on the weight and form of the electro-magnet and armature. He states that A is greater than 1, that B is a fraction, and C lies between 1 and 2. It need scarcely be suggested that the truth of a law enunciated on such indefinite data requires farther confirmation.

Law of Induction of Magnetism in Bars.—Van Rees, of Utrecht, has published(1), a valuable theoretical inquiry on the induction of magnetism in regularly magnetized bars of steel and iron. The ground from which he starts is based upon the hypothesis now almost generally adopted by physicists—that every regular magnet consists of series of magnetically polar particles, which present to each other their dissimilar poles. This assumption, combined with the conception that the action, at a distance or externally, of each magnetic particle is proportional to the amount of its magnetic momentum,—*i. e.*, that it is in the ratio compounded of those of its charge of the free magnetic fluids, and of their interval of separation (the distance of their poles from each other)—conducted him logically to the conclusion, that the charge (y) of the free magnetic fluid distributed over a disc, whose thickness is equal to the unit of length, and which we consider as bounded by two planes, perpendicular to the magnetic axis, and at any distance (x) from the middle of the rod, is equal to the differential quotient $\left(\frac{dz}{dx}\right)$ of the magnetic momentum (z) at that point, considered as a function of the distance x.

In substituting, then, for y the algebraic expression calculated by Biot, on the known observations of Coulomb respecting the distribution of free magnetism on steel wires, (which expression, however,

(1) Pogg. Ann. LXX, 1. (2) Traité de Physique, III, 70.

in order to be adapted to this case, must be referred to the middle instead of to the end of the magnet-bar), he arrived by integration at the equation $z = a - b\ (\mu^x + \mu^{-x})$, which, when the distance x and the moment z are co-ordinates of a curve, belongs to the catenary. The three constants, a, b, and μ, must be determined specially for each magnet.

Law of induction of magnetism in bars.

We may expect that this law, deduced in the first instance from the behaviour of steel magnets, holds good also for electro-magnets, which are surrounded through their whole length, and uniformly, by wire-coils, since the current circulating round the iron bar exerts on all points of it the same magnetizing action, and, so long as it continues, supplies the place of the coercive power, which is wanting in soft iron.

It is now several years since the induction of magnetism in electro-magnets was determined experimentally by Lenz and Jakobi(1). They moved a very small induction-coil, whose wires were connected with a delicate galvanometer, successively over different points of the electro-magnet, and, a galvanic current of constant strength being passed through the electro-magnetic helix, they measured at each point the action which this part of the magnet exerted on the spirals of the induction-coil. The strength of the induced current was assumed to be equal to the sine of half the angle of deflection of the galvanometer-needle, and as an expression proportional to the quantity of the fluid separated at the corresponding point of the magnet. From the values so obtained, these physicists deduced the conclusion, that magnetism is developed under the influence of the current most strongly at the middle of an iron cylinder, that is, precisely where the free magnetism is at zero, and that from this point to the two extremities, the decrease of the magnetic separation follows a law which corresponds to a parabolic curve.

Van Rees remarks, that Lenz and Jakobi have measured, by their method, not exactly the quantity, but the momentum of the magnetic fluid separated at the various points; since, in fact, the strength of the induction is proportional to the quantity of the dissimilar magnetic fluids separated, compounded with the distance through which they must return, to coalesce again at the instant of the opening of the magnetic circuit. These experiments may serve as a crucial test of the law discovered by Van Rees. The latter philosopher has with this view re-calculated these results according to his own formula, and finds that they actually coincide even

(1) Pogg. Ann. LXI, 271, 448.

Law of induction of magnetism in bars.

more closely with it, than with the parabola indicated by the former physicists(1).

Van Rees has, however, made some experiments himself to test the correctness of this law as applied to steel magnets(2). He used for this purpose, as did Lenz and Jakobi, a small induction-helix, which was moved over the magnetized steel-bars, being kept as close as possible to their surface. It was made to traverse, first from the middle outwards, then from points at various distances from the centre, and the momentary current thus produced was measured with the galvanometer. Its strength, assumed as equal to the sine of half the angle of deflection, must be proportional to the quantity of free magnetism which existed in the portion of the bar enclosed between its extremity and the point from which the motion commenced, and is taken as a proportional expression for the magnetic momentum at that point.

Experiments of this kind were made with rectangular prismatic, as well as with cylindrical magnet-bars. The results exhibited generally a satisfactory concordance with the theoretical law. Those of the last observations only of each series, namely, those of the strength of the currents obtained by drawing off the helix from the end of each bar, came out invariably somewhat less than the indications of calculation. For this reason, van Rees does not yet venture to consider the law proposed by himself as altogether proved. Now the discrepancies remarked certainly cannot be accidental, since some of them far exceed the limits of observational error, and, moreover, also occur in the series of experiments of the Petersburg physicists. They seem, however, to be only a result of lateral inductive actions, which, in the methods of experiment selected, were not to be altogether avoided, and which evidently, at the end of the bar, where their influence can only be exerted from one side, must entail a comparatively smaller amount of action. It cannot be doubted, that it is in consequence of similar actions, that the strength of the current always appears somewhat too great when the coil is drawn off from points in the neighbourhood of the magnet-poles.

Van Rees takes, as above remarked, the strength of the momentary current, according to the example of Lenz and Jakobi, to be proportional to the sine of half the angle of deflection. The objection might, however, be raised against the correctness of this assumption, that the first arc of deflection described by the galvanometer-needle, cannot attain its total theoretical magnitude, by

(1) Pogg. Ann. LXX, 20. (2) Ibid. LXXIV 213.

reason of the presence of that induction-current, which its own motion sets up in the spirals; an objection of which the validity cannot be easily decided *a priori*. Van Rees has, however, removed it by means of a series of experiments, in which, comparing the deflections observed, with those calculated (for a given magnitude of electromotive power exerted by induction, under known but variable resistances to conduction), he always found them equal to each other. Law of induction of magnetism in bars.

The experimental confirmation of the law proposed by van Rees, affords also a full corroboration of the law of Biot, of the distribution of free magnetism, which, indeed, forms the foundation of the former. The formula $y = A\ (\mu^x - \mu^{2l-x})$, or, if the origin is taken at the middle of the magnet, $y = -A\,\mu^l\,(\mu^x - \mu^{-x})$, though at first applied only to magnetized steel wires, may be employed with equal accuracy to calculate the distribution of free magnetism on straight magnet-bars of every kind.

Alteration of Form by Magnetism.—We have some experiments by the active physicist, Joule(1), on the influence of magnetization on the form of iron bars. He has found that bars, especially of very soft iron, are lengthened at the instant of magnetization, without, however, any alteration of their volume, so that therefore a proportional diminution of their section must simultaneously occur. During the extinction of the magnetism (f. i., by interruption of the inducing current) the bars do not return perfectly, or, at all events, only very slowly to their original length. The sound known to be given out by iron bars at the instant of the entrance of the current into the coil around it, may be explained by this alteration of form.—Joule puts the elongation of very soft bars proportional to the square of the intensity of the magnetism. In the case of iron hardened, or in a state of tension, as well as of steel bars, the elongation is irregular, and even passes, under very strong tension (such, *e. g.*, as that produced by a suspended weight), into a contraction.

Terrestrial Magnetism.—Lamont(2) has synoptically arranged several determinations of the mean horizontal intensity of the magnetism of the earth, made partly by Langberg, partly by Ångström, and partly by himself. They were all reduced, for better comparison, for the 1st of January, 1845. Below are stated the mean horizontal intensities at—

(1) Phil. Mag. [3] XXX, 76, 225; Arch. Ph. Nat. IV, 398; V, 51, (in abstr.).
(2) Pogg. Ann. LXX, 150.

Terrestrial magne-

Places.	Determinations of: Langberg.	Ångström.	Lamont.
Copenhagen	1·6545	1·6548	—
Altona	—	1·7262	—
Utrecht	—	—	1·7278
Leyden	—	—	1·7234
Cork	1·6486	—	—
London, Greenwich	1·7191	—	1·7250
London, Woolwich	1·7191	—	1·7197
Göttingen	—	1·7849	—
Dresden	1·8377	—	—
Brussels	1·7710	1·7664	1·7662
Aix-la-Chapelle	—	—	1·7810
Bonn	1·8001	1·7926	1·7941
Prague	1·8740	—	—
Mannheim	—	—	1·8568
Paris	1·8372	1·8355	—
Stuttgard	—	1·8969	1·8870
Tübingen	1·9048	1·9011	1·9034
Strasburg	—	1·8909	—
Augsburg	—	1·9299	—
Ulm	—	1·9186	—
Vienna	1·9731	—	—
Munich	1·9386	—	—
Berne	1·9625	—	—
Geneva	1·9837	—	—
Roveredo	2·0317	—	—
Milan	2·0345	—	—
Venice	2·0674	—	—

Lamont finds the magnetic declination, also reduced on the 1st of January, 1845, to be at:

Tübingen	17° 50,'0	Brussels	21° 15,'1	Leyden	20° 47,'3
Mannheim	18° 12,'8	Utrecht	20° 19,'0	London, Greenwich	23° 3,'9

From some comparative experiments on the times of oscillation of a magnet-bar *in vacuo,* and in air of various densities, which Lamont has conducted in concert with Kuhn, it appears that the retardation occasioned by the air, is as great as if the mass of the magnet was augmented by the mass of air which surrounds the surface of the oscillating body to a distance of 4 millimetres in every direction(1).

Diamagnetism. Rotation of the Plane of Polarization by Electro-magnets.—Matthiessen(2) has found, among a great many kinds of glass, twenty-three which, between the poles of the magnet, rotate the plane of polarization more strongly than Faraday's

(1) Pogg. Ann. LXXI, 124.
(2) Compt. Rend. XXIV, 969; XXV, 200; Pogg. Ann. LXXIII, 65, 71; Arch. Ph. Nat. V, 126.

heavy glass. The silicates of lead are remarkable in this respect. Matthiessen has examined the influence of the strength of the electro-magnets, of the distance of the poles, of the inclination of the magnetic axes, of the thickness of the glasses, of their annealing, and of the multiplication of their surfaces, and he gives us a list of his most effective glasses(1).

Diamagnetism. Rotation of the plane of polarization by electro-magnets.

Bertin(2), in an examination of the rotation of the plane of polarization by the electro-magnet, or the wire-helix, has been the first to establish, under various circumstances, the law—that the rotation is always in the direction of the magnetizing current, or of the currents which, according to Ampère, would be set up, under the influence of the electro-magnet, in a piece of soft iron, placed in the position of the substance employed. He takes this opportunity of pointing out, that strong rotations may be obtained by inserting several glasses within a series of coils, which having their axes coincident, conduct the current in the same direction. A very convenient mode of making experiments on the rotation of the pole of polarization by one pole of the magnet, is that of placing a Nörrenberg's polarizing apparatus on the horizontal polar surface of a powerful magnet, the polarizing substance on the lower silvered mirror, and a Soleil's plate of two rotations on the little table, which receives the crystal. The rotation is by these means doubled, the light passing twice through the polarizing substance. A glass of 48^{mm} thickness gave a rotation of 21^{0}.—This arrangement is, moreover, adapted to exhibit the action of the magnet on quartz plates, since the peculiar rotation of this substance is compensated by two opposing effects.

The amount of rotation, under a given strength of current, depends upon the nature of the substance, on the thickness of the lamina employed, and on the distance of the poles. Bertin found, that if one pole only is allowed to act on a piece of flint-glass 39^{mm} thick, and if its distance is made to increase in arithmetic progression, the rotation of the plane of polarization diminishes in geometric progression. Thus, if A is the rotation which the flint-glass exhibits when in contact with the pole, and $A r$ the rotation at 1^{mm} distance, then, at the distance x^{mm}, the rotation $y = A r^{x}$; let then c represent the rotation, produced by a lamina of 1^{mm} thick-

(1) Compt. Rend. XXV, 173; Pogg. Ann. LXXIII, 77.
(2) Ann. Ch. Phys. [3] XXIII, 5; Pogg. Ann. LXXV, 420; Compt. Rend. XXVI, 216, (in abstr.); Instit. 1848, 53; Pogg. Ann. LXXIV, 143.

Diamagnetism. Rotation of the plane of polarization by electro-magnets.

ness, in contact with the pole, then, for a body of e^{mm} thickness, we have:

$$A = c\,\frac{1-r^e}{1-r} \text{ therefore } y = c\left(\frac{1-r^e}{1-r}\right)r^x$$

Thus the action of two poles, which have a distance d, and between which an active body of the thickness e is placed, is expressed by

$$z = c\left(\frac{1-r^e}{1-r}\right)\left(r^x + r^{d-e-x}\right)$$

Let z, z', z'' be the rotations, for the distances $x, x+a, x+2a$, then $\frac{z+z''}{z'} = r^a + r^{-a}$ is a constant magnitude. This result, as well as some others, deduced by Bertin from the formulæ, were most satisfactorily confirmed by observation. The magnitude c varies with the intensity of the magnetism, according to the same law in the case of all bodies, so that the proportions of the values of c are dependent only on the nature of the substances. Bertin proposes to call c the *coefficient of magnetic polarization*, and has determined it for the following substances, assuming it $= 1$ for Faraday's flint-glass:

Guinand's flint-glass	0·87	Terchloride of phosphorus	0·51
Matthiessen's flint-glass	0·83	Solution of chloride of zinc	0·55
Very dense flint-glass	0·55	" " calcium	0·45
Common flint-glass	0·53	Water	0·25
Bichloride of tin	0·77	Common alcohol (36° B.)	0·18
Bisulphide of carbon	0·74	Ether	0·15

Rotation by Magnetism of the plane of Polarization in compressed Bodies.—Matteucci(1) has found, that, if polarized light is passed through crown-glass, flint-glass, and Faraday's heavy glass, the Soleil's quartz-apparatus, which indicates the position of the plane of polarization, being placed at zero, the rotation takes place on these bodies being compressed. If now an electro-magnet is allowed to act upon them, the rotation of the plane of polarization is stronger in the direction of that exhibited under compression than in the contrary direction; while previously to the compression, the rotations, right- and left-handed, under converse currents were equal. Matteucci found farther that the rotation produced by magnets was remarkably increased at higher temperatures, being, f. i., at the temperature of boiling oil, twice as great as at the ordinary temperature.

(1) Ann. Ch. Phys. [3] XXIV, 354.

Action of Magnetism on radiant Heat.—Wartmann(1) has proved in the following manner the action of magnetism on the plane of polarization of radiant heat. A pencil of heat-rays from a Locatelli's lamp is polarized by a bundle of mica, and passes thence through a cylinder of rock-salt, and then through a second bundle of mica, whose plane of polizaration is perpendicular to that of the first. Since the polarization is never perfect, the heat-pencil is always found still to affect a thermo-pile; however, this action is found to increase, as soon as an electro-magnet, whose pole is in contact with the rock-salt, or the current in a helix which encloses it, is set in action,—a proof that the plane of polarization is rotated. The effects are but slight; however Wartmann considers them to be unequivocal. Action of magnetism on radiant heat.

A paper by Airy(2) has appeared on the equations for light under the action of magnetism.

Magnetism as a general Property of Matter.—The facts, independently observed by Brugmans(3) and by Le Baillif(4) connected with the repulsion of bismuth by the magnetic pole, as well as that noticed by J. Seebeck, that bismuth assumes between the poles a position equatorial or perpendicular to the magnetic axis, are now understood, from the extensive researches of Faraday(5), to be expressions of a generally diffused natural force, by which all bodies are either attracted or repelled by the magnet. To the first, or magnetic, class of bodies, of which iron is the type, belong, according to Faraday, nickel, cobalt, manganese, chromium, cerium, titanium, palladium, platinum, osmium, aluminum, as well as all natural and artificial compounds of these metals. Besides these, paper, sealing-wax, indian-ink, porcelain, asbestos, fluor-spar, minium, cinnabar, peroxide of lead, sulphate of zinc, tourmaline, graphite, shellac, and wood-charcoal prove to be slightly magnetic. To the second group of bodies which Faraday names *diamagnetic*, belong bismuth, antimony, zinc, tin, cadmium, sodium, mercury, lead, silver, copper, gold, arsenic, uranium, rhodium, iridium, tungsten, and many compounds of these bodies; as also alum, chloride of ammonium, soda, calc-spar, tartaric acid, citric acid, alcohol, ether, nitric acid, sulphuric acid, hydrochloric acid,

(1) Pogg. Ann. LXXI, 573.
(2) Phil. Mag. [3] XXVIII, 469; Pogg. Ann. LXX, 272.
(3) Pogg. Ann. X, 293.
(4) Ibid. 507.
(5) Phil. Trans. 1846, 41; Phil. Mag. [3] XXVIII, 455; Pogg. Ann. LXX, 24.

Magnetism as a general property of matter.

iodine, phosphorus, sulphur, rosin, wax, olive oil, oil of turpentine, caoutchouc, sugar, starch, gum, wood, ivory.

Plücker(1) has made some observations on certain phenomena dependent on the magnetic, or diamagnetic property of liquids. The distance between the two polar pieces of the electro-magnet being 2·5^{mm}, a watch-glass, cut from a globe of 36^{mm} radius, and so far filled with a solution of sesquichloride of iron, that its surface was bounded by a circle of 35^{mm} diameter, was placed on the polar pieces, so that it touched their extreme points. The circuit being closed, the surface of the liquid seen from above, formed an ellipse, whose major axis, 40^{mm}long, fell in the equatorial plane, and the minor, 25^{mm} long, in the magnetic axis. In the centre the liquid was elevated more than 1^{mm}, so that it formed a convexity about the equatorial plane. The distance of the poles being increased to 8^{mm}, the elliptic form was converted into an oval; and at 15^{mm}, and even more decidedly at 23^{mm}, the longer axis of this figure coincided with the magnetic axis. Solutions of protochloride, and of sulphate of protoxide, of iron and of nitrate of protoxide of nickel exhibited similar, but weaker, actions. If the liquid contained in the watch-glass were diamagnetic, it was seen to extend itself in the axial, and to contract in the equatorial direction, forming a depression about this latter plane. Plücker is of opinion that a method may be founded on the observations here described, not only of discovering the slightest trace of magnetism or of diamagnetism, but also of measuring the strength of both. He proposes the following apparatus for this purpose. An open parellelopipedic box of thin brass is inserted between the vertical surfaces of the polar pieces. Into the lower part of one of those surfaces, which are perpendicular to the equatorial plane, there is cemented a glass tube which rises gradually outwards. The box being filled partly with a diamagnetic or with a magnetic liquid, on the circuit being closed, the level in the glass tube is seen to rise in the first case, and in the second to fall.

If the experiments on the direction assumed by bodies between the magnet-poles, are not conducted *in vacuo*, the results obtained are only relative, *i. e.* a magnetic body may arrange itself equatorially, or a diamagnetic axially, if it is less strongly endued with its peculiar property than is the surrounding medium. We need but remember the observations of Faraday, according to which a

(1) Pogg. Ann. LXX, 567.

solution of green vitriol, enclosed in a glass tube, and immersed in a more dilute solution of the same salt, assumed an axial position; but in a more concentrated, an equatorial. The magnetic behaviour of gases must be conceived entirely under this view, if the experiments cannot be made *in vacuo*. The method of observation adopted by Faraday had indeed prevented him at first from recognizing the magnetism of gases; he believed that they should be placed at the zero-point of the magnetic scale. However, the remarkable phenomena presented by flames between the magnet-poles, which, discovered by Bancalari, and confirmed and pursued into detail by Zantedeschi(1), and by Faraday, led the English philosopher to a new series of researches(2), which elicited unequivocally the diamagnetic and magnetic properties of the gases, which, moreover, have been confirmed in all essentials by Plücker. Faraday passed the gases through a curved tube, into the middle of the space between the polar surfaces, upwards if they were lighter, downwards if heavier than atmospheric air. In the escape-tube was placed a piece of bibulous paper moistened with hydrochloric acid; three receiving-tubes, open at both ends, were placed in the equatorial plane, of which one was vertical, and directly over the mouth of the delivering-tube, the two others being respectively right and left of the axial line, and somewhat inclined outwards; these three, each being provided with a piece of paper moistened with ammonia, served to indicate the direction taken by the stream of gas. Walls of glass surrounded the field of observation so as to exclude interfering currents. A current of nitrogen gas, f. i., sent upwards, passed directly across the axial line into the receiving-tube placed over it. On the magnet being set in action, part of the gas-current immediately appeared in the side-tubes. If the stream passed, at first, somewhat at the side of the axial line, it was deflected entirely by the magnetic action into the nearer lateral tube, being repelled in an equatorial direction,—it therefore behaved as a diamagnetic in atmospheric air. Hydrogen, carbonic acid, carbonic oxide, protoxide, binoxide, and teroxide of nitrogen, olefiant-gas, coal-gas, sulphurous, hydrochloric, and hydriodic acids, terfluoride of silicium, mercury-vapour, steam, ammonia, chlorine, iodine, and bromine.—A stream of of oxygen, which, in the air, passed downwards between the poles,

Magnetism as a general property of matter.

(1) Phil. Mag. [3] XXXI, 421; Pogg. Ann. LXX, 286; Instit. 1848.
(2) Phil. Mag. [3] XXXI, 401; Pogg. Ann. LXXIII, 276; Instit. 1848, 13, 24.

Magnetism as a general property of matter.

was made, by the influence of the magnet, to approach the axial line. Oxygen, therefore, behaved magnetically in atmospheric air. This property seems to be still active in its combinations with nitrogen, since these appear to be less strongly diamagnetic than pure nitrogen. Faraday found, on substituting other gases for the air surrounding the gas-current, that atmospheric air, oxygen, and binoxide of nitrogen appeared magnetic in carbonic acid, in which, on the contrary, nitrogen, hydrogen, coal-gas, olefiant-gas, hydrochloric acid, ammonia, carbonic oxide, and protoxide of nitrogen were diamagnetic. In coal-gas, common air, oxygen, and even nitrogen are magnetic; in hydrogen, air and oxygen are magnetic, the other gases being diamagnetic.

Faraday ascertained, by placing in the mouth of the escape-tube, a spiral platinum wire, which could be heated at pleasure by the electric current, that, by raising the temperature, the diamagnetism of the gases could be exalted. A hot stream always behaved as decidedly diamagnetic in a colder medium homogeneous with itself. By this single experiment, all the phenomena of flames observed, and repeatedly varied by Zantedeschi, by Faraday, and by Plücker, are explained. If the flame stands near the axial line, it is driven into an equatorial position by the magnetism, the flame being so much the more compressed between the poles as these approach more nearly to each other. It expands itself in the form of a fish-tail, and at last becomes cloven into a bifurcated form. The flames serve but to render visible the diamagnetic deportment of the hot current. The same phenomena are observed, in even greater regularity, with the smoke-current of a smouldering taper, of a pastile, or of the flame of oil of turpentine.—Incidentally to his researches on the diamagnetism of gases, Plücker(1) describes an experiment on the diamagnetism of gases, which seems to him to prove that the air in the neighbourhood of the pole becomes rarified by the repulsive power of the magnet. He placed between the poles a vessel of brass plate, which fitted tightly upon their surfaces, so that it occupied the entire space between them. The vessel was closed air-tight, a glass-tube of 1^{mm} diameter, being let into the centre of one of the side-surfaces, in a horizontal direction. By a drop of alcohol placed in this tube, the enclosed air was separated from the outer atmosphere. The magnetism was now excited by 12 of Grove's cells, at the same instant the alcohol-drop

(1) Pogg. Ann. LXXIII, 579.

moved 3^{mm} towards the mouth of the tube, and instantly returned to its former position on the voltaic contact being broken. Magnetism as a general property of matter.

Plücker(1) has employed a peculiar method of his own to compare the magnetic power inherent in equal weights of different substances, and to observe its alterations under varying temperatures. A watch-glass is filled with the substance to be examined, of which all excess is removed by sliding over it a ground glass plate, which forms a close cover to the watch glass. It is set in a thin ring of brass, which hangs from one end of the beam of a balance, in which there is no iron except at the axis. The watch-glass rests on the two rounded ends of the polar pieces of an electro-magnet, on a single point of each. If it is filled with a magnetic substance, it is attracted on the induction of the magnetism; the scale hanging at the other extremity of the beam is now charged with fine sand or small bits of paper, until the watch-glass is detached from the poles; the weight of the counterpoise thus added is in each case the measure of the magnetic force. The watch-glass and the brass ring together, form a magnetic system, which is attracted, more weakly, however, when filled with a diamagnetic substance. The diminution of the attraction gives in this case the measure of the diamagnetism of the substance under experiment.—The magnetic and diamagnetic bodies are placed in the watch glass, either in solution, or as powder mixed with lard to a homogeneous mass. In this manner the proportions of the magnetic powers, for equal weights, or for the equivalent weights of the bodies, may be measured, provided that the substance is not so closely packed, that the magnetic induction of the particles on those next to them can exert any appreciable influence; for only in this case can the total attraction be proportional to the number of attracted molecules. The total attractions of the magnet on four solutions of protochloride of iron, in which the quantities of the uniformly distributed magnetic substance were in the ratios 8 : 4 : 2 : 1, were found to be in exactly the same numerical proportion, so that, here, it is evident that no disturbing actions of induction were introduced. Experiments with iron filings, which were placed in the watch-glass, at first, alone, then mixed with lard, proved that the inductive actions, where they occur, diminish the total attraction, provided that the scale-pan touches always the surfaces of both polar pieces. We select the following(2) from his numerous results :

(1) Pogg. Ann. LXXIV, 321; LXXV, 177; Arch. Ph. Nat. IX, 308.
(2) Ibid. 343, 353, 356.

Magnetism as a general property of matter.

MAGNETIC ATTRACTION FOR EQUAL WEIGHTS.

Iron	100000
Magnetic iron ore	40227
Sesquioxide of iron, I.	500
″ ″ ″ II.	286
Hydrated sesquioxide	156
Green vitriol	78
Nitrate of sesquioxide of iron (satur.)	34
Hydrochloric acid	98
Sulphuric acid	58
Sesquioxide of iron dissolved in Nitric acid	287
Sesquioxide of iron dissolved in Hydrochloric acid	516
Sesquioxide of iron dissolved in Sulphuric acid	332
Iron in a solution of sulphate of sesquioxide of iron	474
Protoxide of nickel	35
Hydrate of protoxide of nickel	106
″ ″ sesquioxide of manganese	70
Proto-sesquioxide of manganese	167
Manganese in its proto-sesquioxide	232

The dissimilarity of these values for the sesquioxide of iron prepared in various ways, sufficiently proves the irregularity of the results. Plücker ascribes the discrepancy to the presence of protoxide; being, however, still uncertain what number should be considered as corresponding to pure sesquioxide of iron. Since the magnetic power of a chemical compound may be considered either as belonging to the compound as such, or only to one of the constituents in the pure state, we must consider under this view the magnetic forces represented in the above table, f. i., those calculated for the sesquioxide of iron, and for the iron in the saline solutions. Plücker points it out as especially deserving of attention, that, in the solutions of the salts, the original magnetism of the sesquioxide is not weakened by the association of the acid, that the magnetism of the protoxide of nickel is increased about fourfold by the addition of the water of hydration, and that in the case of manganese the proto-sesquioxide, which is formed by the ignition of the hydrated sesquioxide, is considerably more magnetic than the hydrate, as is also the case with the corresponding iron-compounds.

DIAMAGNETIC REPULSIONS FOR EQUAL

	Volumes.	Weights.		Volumes.	Weights.
Water	100	100	Satur. solution of ferrocyanide of potassium	86	70
Alcohol I. (0·813)	93	114	Purified chloride of sodium, powdered	—	79
Alcohol II. (0·851)	122·5	143	Teroxide of bismuth, powdered	—	35
Ether	93	127	Sublimed sulphur	—	71
Bisulphide of ca bon	129	102	Oil of turpentine	107	123
Sulphuric acid	64	34	Mercury	314	23
Hydrochloric acid	114	102	Phosphorus	172	100
Nitric acid	71	48			
Ox-blood, beaten up	122·5	—			

It is difficult to understand on what grounds Plücker inferred from these experiments and their results, that a simple relation exists among the numbers of the second column in the above table.

Magnetism as a general property of matter.

It was considered, till lately, as an established fact, that the magnetism of steel magnets was entirely destroyed by a white heat, and that at this temperature, even iron no longer obeyed the attraction of the magnet. Pouillet, indeed, had stated that cobalt remained magnetic even at a very high temperature, but that, on the contrary, the magnetism of chromium disappeared at a heat somewhat below redness, that of nickel at 350°, and of manganese, at 25° or 20° below 0°. Recently, however, Faraday has found by experiments with powerful electro-magnets, that even white-hot iron, and nickel heated far above 350°, still followed the attraction: and Plücker(1) has more closely examined the behaviour of the magnetic and diamagnetic properties under increasing temperature. A porcelain scale-pan suspended from a balance, precisely in the manner above described, over the two polar pieces, was filled with the substance, and heated, and during the cooling the weight necessary to detach it was frequently determined, while the temperature was read off from a thermometer immersed in the substance. The experiments with nickel extended over temperatures from 340° to 32°; those with bismuth from 311° to 148°. The behaviour of these metals may be taken as typical, respectively, of the two classes of magnetic bodies. The curve, of which the abscissæ are formed by the temperatures, and the ordinates by the intensities of the attraction, is, for nickel, at high temperatures convex to the axis of the abscissæ, which forms an asymptote to it,—a condition which is irreconcileable either with an absolute extinction of the magnetism, or with a transition to diamagnetism. At 350°, the magnetic force of nickel is at least 35 times less than at 50°. The magnetism decreases most rapidly between 225° and 300°; at 275° the curve has a point of flexure, and is therefore, at lower temperatures, concave towards the axis of the abscissæ. The diamagnetic curve of bismuth is very similar to the foregoing, only that the rapid decrease of the force occurs here within narrower limits, between 245° and 255°.

Faraday considered that it might be concluded from his experiments, that by an appropriate mixture of magnetic and diamagnetic substances, a perfectly neutral body might be produced; Plücker(2), however, has been led by his observations to an opposite conclusion. A piece of carbon assumed an equatorial position between the polar points, when placed as close together as possible, but an axial, when

(1) Pogg. Ann. LXXV, 177.
(2) Ibid. LXXII, 243; LXXIII, 617; LXXIV, 362; LXXV, 413.

Magnetism as a general property of matter.

they were farther separated. With a certain arrangement of the pole, the carbon placed itself axially, when the current proceeded from a single Grove's cell; it took up a determinate mean position, at an angle of 40° with the axis, when three cells were used; with seven it stood exactly equatorially. A piece of bismuth suspended in equilibrium in a balance at a distance of 3·5^{mm} was repelled diamagnetically, when the magnetism was induced by the action of eight cells, with four it was magnetically attracted. When a single cell was employed, the magnetic power was considerably stronger. Plücker concludes from these experiments, that the diamagnetism increases more rapidly than the magnetism, with an increasing power in the electro-magnet; and he considers it to be quite indifferent, whether the increase of the intensity arises from the employment of a greater number of cells, or from a closer approximation to the poles. If these results are perfectly accurate, no absolutely neutral body can exist: for a body which behaves as neutral at any given distance, will be magnetic at a greater, diamagnetic at a less distance.

The following experiments of Poggendorff and Weber(1) have proved that diamagnetic repulsion can be exerted by the galvanic current, even without the intervention of iron; they offer at the same time a means of absolutely measuring the diamagnetic power. For these experiments a wire-coil was used, which being adapted especially for other objects, did not combine exactly the conditions most convenient for diamagnetic observations. A copper wire, one Parisian line in thickness, and weighing three hundred pounds, was wound on a wooden reel of 600^{mm} diameter, and 200^{mm} length, so that the innermost spiral contained 1900^{mm} of wire, and the outermost 2350^{mm}. In the interior of the coil a bar of bismuth of 308·6 grammes weight, 14^{mm} thickness, and 210^{mm} length, was suspended by some fibres of unspun silk, so that it formed an angle of 45° with the plane of the convolutions of the coil, which was placed parallel to the magnetic meridian. One end of the bar carried a plane mirror, in which the image of a scale 2340^{mm} distant was observed by means of a telescope. The oscillations of the needle having been observed for some time, and it having been found that the position of equilibrium was variable, quite independently of magnetic influences, the helix was connected with a Grove's battery of twenty-four cells, in which platinized lead

(1) Berl. Acad. Ber., August, 1848; Instit. 1849, 60.

was substituted for platinum, the nitric acid being mixed with a strong dose of sulphuric acid; the contact was maintained till the bismuth bar had completed two oscillations. During the two next oscillations the circuit was opened, and so on alternately. The mean of several experiments shewed an approach of 44·545 divisions of the scale, or $0^0{\cdot}32'$, of the position of equilibrium of the bismuth bar to the plane of the convolutions, whereby the diamagnetic action of the galvanic current was unequivocally proved. The duration of the oscillations of the bar was 168 sec., its momentum of inertia, taking the millimetre and the milligramme as the unit, $k = 1{,}176{,}000{,}000$, therefore, the directive force of the needle $D = \frac{\pi^2}{t^2} k = 411{\cdot}400$, and the deflecting force of the current $F = \frac{44{\cdot}545}{4694} D = 3903$; (the distance of the graduated scale from the mirror was 2347 divisions of the scale).—This deflecting power is equal to the product of the diamagnetic momentum of the bismuth rod, Δ, into the sine of the angle φ, which it makes with the axis of the coil, and multiplied by the product of the momentum of action Γ of the galvanic current, on a body in the centre of the coil, into the cosine of the angle φ.—We have, however, $\Gamma = \frac{2\,G}{R^3}$, if G denotes the galvanic momentum of the current and R the semidiameter of the coil; and since R has been found $= 340^{mm}$, and G, by the known method from the deflection of a magnet-needle, $=$ 1,170,000,000,000, $\Gamma = 596$, and, from the equation $\Gamma\,\Delta$ sin. ϕ cos. $\phi = 3903$, we get $\Delta = 13{\cdot}1$. To the unit of the galvanic momentum corresponds then a diamagnetic momentum $\delta = \frac{13{\cdot}1}{596} = 0{\cdot}022$, and, therefore, for the weight-unit of bismuth, we have a momentum $= \frac{1}{14{,}000{,}000}$, while $1^{m{\cdot}gr.}$ of strongly magnetized steel contains about four hundred magnetic units. The horizontal component of the terrestrial magnetic force being $= 1{\cdot}84$, it produces in the weight-unit of bismuth a diamagnetic power about 3000 million times weaker than the magnetic power of the weight-unit of strongly magnetized steel.

Magnetism as a general property of matter.

Faraday had, indeed, expressed the opinion that the excitation of diamagnetism might depend upon the induction of electric currents; however the apparently perfect absence of true polarity in diamag-

Magnetism as a general property of matter.

netic bodies led him to reject this notion. Only after Reich(1) had shewn that diamagnetic substances were really repelled from either pole of a magnet taken separately, but, that, when both poles were employed together, only the difference of their power exerted any action,—did Weber(2) return to the above-mentioned opinion of Faraday on the origin of diamagnetism; and he now succeeded in proving, in the following manner, the polarity of diamagnetized bodies. He placed a piece of bismuth in the plane, which bisected at right angles a small symmetrically magnetized needle, suspended from a cocoon-silk fibre, so that the poles of the needle had no sensible influence on the diamagnetic state of the piece of bismuth, which was fixed at some distance from it. He then placed a strong horse-shoe magnet, so that the place already occupied by the bismuth lay in the free space between its two poles, and so that its magnetic axis bisected the needle. The momentum of rotation due to the horse-shoe magnet was directly compensated by a magnet-bar placed in opposition to it, so that the needle was free to obey the action of the terrestrial magnetism. If now the piece of bismuth was moved downwards between the poles, the needle was immediately deflected; if the poles of the magnets, whose actions on the needle were mutually compensated, were reversed, the bismuth, at the same place, and in the same position, now produced the opposite deflection. If iron was substituted for the bismuth, the deflections were now, under similar circumstances, exactly the converse. Poggendorff(3) and Plücker(4) have also described experiments which go to prove the polarity of diamagnetic bodies. Poggendorff recommends among other means, a small bar of bismuth, suspended between the poles of an electro-magnet, within a cylindrical wire-coil, whose axis is directed equatorially. So long as the electro-magnet is out of action, a current passing through the coil does not affect the bismuth; but as soon as the electro-magnet is excited, a deflection to the right or left, according to the direction of the current, is observed. The bismuth bar is, therefore, under these circumstances, transversely magnetic in the equatorial position, so that the poles of the bismuth are presented to the analogous poles of the magnet.

A peculiar action of the magnet-poles, on bodies of organic structure, as well as on the optically uni- and bi-axial crystals,

(1) Pogg. Ann. LXXIII, 60; Phil. Mag, [3] XXIV, 127; Instit. 1849, 119.
(2) Ibid. 241. (3) Ibid. 475. (4) Ibid. 613.

has been discovered by Plücker(1). Bodies of organic texture place the axes of their grain, as, f. i., the direction of the fibre of wood, &c., equatorially. Experiments with tourmalines, with double-refracting spar, rock-crystal, zircon, beryl, emerald, idocrase, and corundum, prove the existence of a repulsive action, which is directed upon the optic axes of these uniaxial media, and is always exerted if it is not masked by a predominating magnetic attraction. Experiments with mica, which behaves magnetically, and with topaz and sugar, which are diamagnetic, showed that there is an equal repulsion of the axes of optically biaxial crystals. In the case of Brazilian topaz, arragonite, saltpetre, Glaubers' salt, &c., which are diamagnetic, and crystallize in prisms, whose axis coincides with the optic medial line, diamagnetism concurs with the repulsion of the axis, in determining an equatorial position. However, Plücker ascertained distinctly the presence of the latter by the variation of the torsion-moment, which occurred according as the suspending fibres hung perpendicularly to the plane of the optic axes, or as they lay in this plane in the direction of the medial line, or of the supplementary line. Plücker has shown with a crystal of staurolite, that, in a perfectly opaque crystal, whose external form is entirely obliterated, the position of the optic axes may be discovered by means of the magnet. He(2) farther found that a glass cylinder rapidly cooled, comports itself between the magnet-poles as a uniaxial crystal,—the axis of the cylinder assuming the position of the optic axis.

Magnetism as a general property of matter.

Oersted(3), in a research on diamagnetism, has confirmed many of the earlier additions to our knowledge in this direction, especially the observation of Plücker, that the same bodies which arrange themselves equatorially between the poles when sufficiently near to each other, assume the axial position when they are raised above or placed below the axial line, or even when the poles are removed to a certain distance from each other. Oersted states that diamagnetic actions are also observed in bodies whose entire mass is attracted by the pole, that is, in such as have been hitherto considered as magnetic. Oersted is therefore inclined to divide diamagnetic bodies into such as are attracted, and such as are repelled; of the first he observes, that in the neighbourhood of one of the polar edges they arrange themselves parallel to it,

(1) Pogg. Ann. LXXII, 315. (2) Ibid. LXXV, 108.
(3) Ann. Ch. Phys. [3] XXIV, 424; Phil. Mag. [3] XXXIV, 81; Pogg. Ann. LXXV, 445; Instit. 1848, 326, (more at length), 1849, 92; Arch. Ph. Nat. X, 49.

Magnetism as a general property of matter.

that the induction of the magnetic power is transverse in them, as in diamagnetic bodies generally, with this difference however, that the poles of the needle are directed towards the electromagnet-poles of the opposite denomination.

The theory of diamagnetism is, as may be readily conceived, not yet elaborated. Weber(1) has subjected to an experimental test the opinion that the induction of diamagnetism depends upon molecular currents. If the currents of Ampère are present in diamagnetic bodies, which are moved or rotated under the influence of a strong magnet; then, at the moment of this action, a current must be induced by them in neighbouring conductors, which indeed must be extremely weak, and can only be observed if the power of the strong magnet is constant, so that no disturbing inductive action should occur. Upon the circular terminal surface of a straight iron core was placed an induction-coil of 300 metres of copper wire, enclosing a space 140^{mm} long, and 15^{mm} wide. A bar of pure bismuth fitted into this space, and, the iron core being kept in as constant action as possible, was alternately pushed down into it, and drawn out; while the commutator, to which the extremities of the induction-coil passed, was each time inverted; the wires of a sensitive galvanometer terminated in the same commutator. In a second series of experiments, the commutator was placed in positions exactly the converse, on the entrance and removal of the bismuth bar. In a third series the positions of the first were repeated, and so on. The comparison of the mean value of the results of each different series from the second to the sixth, with the mean of those immediately preceding and succeeding it, gave the following results :—

2. 514·02 = 516·82 — 2·80
3. 518·72 = 515·53 + 3·19
4. 517·04 = 520·36 — 3·32
5. 522·00 = 518·47 + 3·53
6. 519·90 = 525·43 — 5·53

which place beyond doubt the induction of a current through the bismuth, since the mean value for the one position of the commutator is, throughout, invariably greater than for the other. Counter experiments, with a small iron bar, showed that bismuth and iron, under similar circumstances, induce opposite currents, whence it follows, that the molecular currents also in the bismuth are in a direction opposite to those in the iron. The reason why these

(1) Pogg. Ann. LXXIII, 217.

currents circulate in diamagnetic bodies in opposite directions to those in magnetic, is certainly still in obscurity. Weber thinks that, whereas hitherto only already existing molecular currents have been considered, to which the induction gives a uniform direction, we may assume, for the explanation of the phenomena of diamagnetism, the excitation of molecular currents, which, once set up, continue until they are cancelled by the action of a new antagonist induction.

Magnetism as a general property of matter.

Zantedeschi(1) reports—1stly, that magnetism is far more diffused over inorganic nature than Faraday has assumed; 2ndly, that all organic bodies are diamagnetic; 3rdly, that repulsion between molecules depends on diamagnetism, and 4thly, attraction between them on magnetism; that, therefore, chemical combinations of magnetic elements must be much more stable than of diamagnetic.

A treatise by De Haldat(2) enlarges upon the universality of magnetism.

ELECTRICITY.

Conducting Power of Flame.—It has been long known, that flame possesses a property subversive of electricity. Whoever is engaged in electrical experiments avails himself of this property, to rid plates of resin, and handles of glass or shellac, of adhering electricity. With respect to the cause of this behaviour, the labours of distinguished physicists for upwards of one hundred years have only established thus much,—that flame possesses a very strong conducting power for electricity, which can neither be explained merely by the rise of temperature of the air, nor by any conducting property of the aqueous vapour contained in the hot air of the flame, nor by a current of air, or a removal of electricity by the volatile particles that rise from the flame; for not one of these influences by itself evinces the conducting-power in so high a degree as flame. However, Volta made use of the flame of a lamp to draw electricity from the air, and collect it in his condenser.

(1) Instit. 1848, 102.

(2) Compt. Rend. XXII, 739; Instit. 1846, 113; Ann. Ch. Phys. [3] XIX, 113; Phil. Mag. [3] XXX, 319.

Conducting power of flame. A few years since, Riess(1) observed that the action of flame extends over much greater distances than does the upward current of hot air, or than this could make the air conductive; and that it extends in directions (f. i. laterally from the flame) in which this current does not move at all. From this he concluded that the flame acts not only by direct communication, but also by induction (influence), and hence endeavoured to reduce the effect of flame to that of points. He started from the consideration, that the current of hot gas ascending from the flame, and conducting the electricity, was repeatedly cut into and divided by the cold air (which does not conduct electricity) streaming upon and penetrating it, so that there are formed points and threads as it were of the conducting gas, which become more and more attenuated, and are gradually dispersed through the air under the influence of the colder surrounding medium. These serrations and points now exert their powerful influence in inducing electricity in all directions and to considerable distances, producing by this means precisely the effects of good conductors.

The action of points is also exhibited by substances that do not burn with flame, but merely smoulder, as tinder, slow-match, wicks or pastiles; Riess proves, however, that in this case, when they cannot be caused by the ascent of incandescent gases, they originate in the combustion at the surface of the body itself(2).

Several objections that had been made by van Rees(3) against the mode of explanation given by Riess, have led, within the last two years, to a scientific dispute between these two physicists, in which the latter had the advantage, and which has considerably increased the probability of his explanation(4).

Means of Insulation.—According to communications of Matteucci(5) the insulating property of dry gases diminishes perceptibly even within the interval of temperature from —10^0 to + 20^0.

Shellac and sulphur likewise commence to conduct electricity even at 25^0—30^0.

Riess(6) has remarked that shellac-sticks, freshly prepared, retain electricity much better than after a few days. This results from the agency of the atmosphere and from other inevitable influences on

(1) Berl. Acad. Ber. Febr. 1844; Pogg. Ann. LXI, 543.
(2) Pogg. Ann. LXI, 558.
(3) Het institut of verslagen, etc. 1846, 62.
(4) Pogg. Ann. LXXI, 568; LXXIII, 41, 307; LXXIV, 879, 580.
(5) Compt. Rend. XXV, 324, 935.
(6) Pogg. Ann. LXXI, 372.

Means of insulation.

the surface of the shellac. The use of the sticks, their repeated exposure to the point of the spirit-flame—to make them non-electric—also tends to hasten the deterioration. Such sticks as have become unfit for use may be restored perfectly to their original state by washing them with alcohol. For this purpose they are slightly moistened with strong alcohol (spec. grav. 0·81), wiped with a linen cloth, passed through a flame, and left to dry in a glass bell.

Until lately we were almost exclusively restricted to the use of shellac for efficient insulation, as glass, or even silk, very easily become conductive by reason of their property of attracting moisture from the air. Within the last year (1848), Faraday(1) has drawn the attention of physicists to the highly insulating power of gutta percha, which not only possesses this property under ordinary circumstances, but likewise retains it under atmospheric conditions which would make the surface of glass a good conductor. A good piece of gutta percha insulates as perfectly as shellac, whether it be in the form of a disc, a stick, or a thread. It is, moreover, tough and pliable in the cold, soft in the heat, and hence preferable in many cases to the brittle shellac. In the form of straps or cords, gutta percha presents an excellent means of suspension, and in plates it furnishes the best insulating supports. It forms excellent insulating stoppers for the ends of gold-leaf-electrometers if enclosed in tubes; larger stoppers furnish good insulating stuffing for temporary electrical arrangements. Cylinders of half an inch or more in diameter, possess great rigidity, and form excellent insulating supports. This good insulation, moreover, fits it admirably for exciting negative electricity.

All the gutta percha of commerce does not insulate equally well. If, however, a conducting-piece be warmed in a current of hot air, or in a glass over a spirit-lamp, then spread out and kneaded for some time between the fingers, as though the moisture it contains were to be pressed out, as good an insulator as possible is obtained.

A degree of insulation no less than that of gutta percha is possessed by collodion,—the residuary substance obtained by the evaporation of an ethereal solution of gun-cotton. If the clear solution be spread over a glass plate, there remains, after entire volatilization of the solvent, a transparent cuticle, which, by merely passing the hand over it, or, more effectually, by friction with wool, becomes negatively electric, and obstinately retains this electrical

(1) Phil. Mag. [3] XXXII, 165; Pogg. Ann. LXXIV, 154.

Mes insulation. state. With regard to its chemical constitution, it is identical with the electric paper first prepared by Schönbein(1). Balloons of collodion (see article on this subject) are particularly adapted for the institution of the fundamental experiments on electrical attraction and repulsion.

Electrometry.—A few years ago, Riess made known some electrical measurements(2), which he had obtained by Coulomb's torsion-balance. At that time, he pointed out that the management of this important instrument (which since Coulomb's time has been little used, but found fault with by many on account of various imperfections) was by no means so difficult, nor the attainment of good and concordant results with it by any means so uncertain as many physicists, from prejudice, and frequently, perhaps, in consequence of imperfect construction of the apparatus, appear to believe. In an instructive Memoir, "On the determination of electric densities by the torsion-balance"(3), he returns once more in detail to this subject. He discusses the different methods of determination that may be employed, and the calculations occurring with them, and shows the degree of certainty of each separately. He enumerates the various arrangements and precautionary measures which secure the success of the experiments, and by which the numerous influences, on which depends the more or less rapid dispersion of the electricity communicated to the test-body, may be, if not entirely eliminated, at least referred to their causes and taken into account. A very complete description, illustrated by plates, of the torsion-balance employed by Riess, will facilitate the construction of similar instruments in any place.

R. Kohlrausch(4) of Rinteln gives a minute description of an electrometer constructed by him, according to Oersted's(5), and to Dellmann's(6) principles, improved however in several points, by which, without any loss of delicacy in its indications of electricity, it becomes at the same time a real measuring instrument. The apparatus is actually nothing but the torsion-balance, differing however from the usual one of Coulomb, by being more adapted to measure electricities of low tension, but available in large quantities (f. i. the tension at the poles of a voltaic battery); while the latter is preferable

(1) Pogg. Ann. LXVIII, 159.
(2) Berl. Acad. Ber. Febr. 1844.
(3) Berl. Acad. Ber. 1847, 148; Pogg. Ann. LXXI, 359.
(4) Pogg. Ann. LXXII, 353; LXXIV, 499.
(5) Ibid. LIII, 612.
(6) Ibid. LV, 301.

for measuring the effects of very small quantities of electricity of great intensity. The more minute arrangement of the apparatus cannot be rendered intelligible without a drawing. Electrometry.

Condenser.—Kohlrausch(1) combines with this instrument a peculiarly constructed condenser, which is certainly somewhat complicated, though apparently well adapted for arriving at comparable results, and therefore useful; by its aid, he has succeeded in measuring the electric tensions of simple voltaic circuits with the same accuracy with which their electromotive powers may be determined. Kohlrausch found the electric tension of the open voltaic pile, the number of elements being gradually altered, very accurately proportionate to the number of the elements employed(2). He has likewise measured the electric tension of various closed constant circuits at the moment of breaking contact, and compared with it the simultaneous electromotive power, which was likewise measured. He found, as anticipated, the most perfect proportionality between the two series of experiments(3).

Kohlrausch recommends, for preserving the plates of the condenser out of conducting communication, the old form of appliance already described by Volta, viz. that of three insulating points. For this purpose both plates are provided, at three corresponding points near the margin, with a film of shellac varnish. Small thin pieces of shellac are then melted on to the lower plate at the three places by application of heat below the plate, and after cooling, shaved off as much as requisite by means of a sharp knife. The arrangement must be so made, that both plates are always in contact with each other in exactly the same position, and that the upper one may be lifted off quite parallel from the lower one. According to Kohlrausch, by this arrangement, the condensing power could be increased to 260 times the quantity of electricity that the collector-plate, separated from the condenser-plate, was capable of taking up from the same source.

To perfect the theory of the condenser, Riess(4) has conducted a very elaborate experimental research. The apparatus which he employed consists of two plane brass discs 81·6 par. lin. in diameter, $\frac{17}{24}'''$ thick, with the margins rounded off. They are provided on the central point of one surface with cylindrical arms, terminating hemispherically, of $14\frac{3}{8}'''$ length, and $11\frac{7}{24}$ thickness. These arms are perforated through the axes, so that a conducting channel may be fixed

(1) Pogg. Ann. LXXV, 88. (2) Ibid. LXXV, 94.
(3) Ibid. LXXV, 220.
(4) Ibid. LXXIII, 367; Berl. Acad. Ber. 1847, 465; Instit. 1848, 217.

Condenser. therein by means of a binding screw, and have, at right angles with the axis, a hollow into which is connected a glass rod 8″ 2‴ long, covered with shellac. The discs are fastened perpendicularly on a board by means of these glass rods and appropriate feet. The one, the condenser-plate, moves on a hinge, by which means it may be turned from the vertical position to one below the level of the stand; the other disc, the collector-plate, stands on a slide, traversing on a horizontal prism, which is provided with a scale, and on which it may be fixed at will. The free surfaces of the discs could thus be brought into contact, and removed from each other in the direction of their axes; they form, therefore, when apart, a condensing apparatus, in which the insulating layer consists of air. When in use, the arm of the condenser-plate was provided with a horizontal brass wire, terminating in a small ball, which could be placed in conducting connection with the ground. After the collector-plate had received electricity, the condenser-plate was moved down, and the condensation, *i. e.* the altered arrangement of the electricity on the first plate, cancelled.

A copper wire of ½‴ thickness, and 8″ 5‴ length, fixed to the arm of the collector-plate, leads to a brass ball of 7‴ thickness, resting on a separate glass foot, covered with shellac, and forming the end of the conducting-wire of the collector-plate. If the latter, standing alone or opposite to the condenser-plate, was charged with electricity, the fluid began to escape into the air, at different intensities of charge, according to the condition of the air, but always first from the ball, so that the electric density on the latter, at which the emanation commenced, always denoted the maximum charge of the instrument.

Electricity was now imparted to the collector-plate, by touching the extreme point of the ball with the knob of a charged Leyden jar(1), the electric intensity at the same point of the ball being measured with the torsion-balance, first when the collector-plate stood alone, and then with the condenser-plate at different distances from it. The gradual loss of electricity, during the performance of these experiments, was taken into account according to the method described by Riess(2), in his Memoir on the Torsion-Balance.

Thus, for instance, the intensity, while the condenser-plate was removed, being taken as unit, the following numbers were found:

Distance of the plates	∞	50‴	20‴	15‴	10‴	5‴	4‴	3‴	2‴
Intensity at centre of collector-plate . .	1	0·897	0·683	0·595	0.492	0·335	0·286	0·235	0·173
Intensity at the edge	1	0·941	0·828	0·731	0·617	0·460	0·412	0·341	0·260

(1) Pogg. Ann. LXXIII, 388. (2) Ibid. LXXI, 366.

The condensing power, due to any given distance of the plates, is equivalent to 1 divided by the number representing the corresponding intensity; *e. g.* the intensity 0·173, being contained about 6 times in 1, indicates that the collector-plate can take up about 6 times as much electricity with the condenser-plate at 2‴ distance, as if the latter were entirely removed. Condenser.

It is evident that the intensity, which is inversely proportionate to the accumulation, increases in slower progression than does the distance, and the difference of the ratios is greater, the greater the distances. At very small distances, therefore, the relation of the condensing power to the thickness of the condensing layer will approach more nearly to an inverse proportion.

At the margin of the plate (if the electricity to be tested is taken from it) for equal distances a greater intensity is always shown, than at the ball in connection with the centre. The power, therefore, of a condenser is expressed by a lower number, if the electric body to be examined is brought in contact with its margin, than if with the conductor attached to the centre. The length, too, of the conducting-wire which connects the arm with the ball, is not without its influence. Riess found that a piece of wire of only 3·5‴ length, inserted instead of that of 8″ 5‴, produced a sensibly better condensation. With a still longer wire the diminishing influence of the length ceases to be perceptible.

Riess has also compared the accumulative power of larger and smaller condenser-discs, and confirms the observation of Munck af Rosenschöld(1), that the capability of the larger discs of collecting a greater quantity of electricity from the same source, not only arises from their taking up more when standing alone, but likewise from their possessing a condensing power, which increases with their size.

If, for instance, we combine two small collector-discs, which, standing alone, are capable of receiving the same amount of electricity as a larger one, and then adjust the condenser-discs at equal distances, in each case we shall find that the large condenser is able to contain a much larger quantity than the two small ones together.—Hence the advantage of batteries consisting of a few large jars over those which have a greater number of jars of the same aggregate extent of surface. The less the distance between the discs, the greater is the preponderance of the large condensers over the

(1) Pogg. Ann. LXIX, 44, 223.

Condenser. small ones; this, however, disappears altogether at a considerable increase of the distance.

Discharge by Cascade.—Franklin was the first to propose, that the electricity which passes off from the external coating whilst the inner coating of a battery is charged, should be employed to charge a second battery; he recommended the graduated method (by cascade) as a means of charging a large number of jars with only a few turns of the machine. For this purpose the jars have to be connected by their alternate surfaces (stepwise), and then, after the charge is effected, all the internal surfaces are to be connected together, and likewise all the external, before making a discharge.

Dove(1) now shows experimentally, that there is no necessity for changing the first-mentioned arrangement of the jars; but that if the first internal, and last external coating of a row of jars, connected stepwise, be brought into contact, a result is produced as powerful as if the discharge were effected after connecting all the internal and all the external coatings; although in the latter case we must have a re-combination of almost quadruple quantities of electricity.

The graduated discharge is in fact composed of a series of discharging currents. Let there be, for instance, four jars of equal size; i_1, i_2, i_3, i_4 their internal, e_1, e_2, e_3, e_4 their external coatings; let e_1 and i_2, e_2 and i_3, e_3 and i_4 be respectively placed in contact during the charge, by means of a copper wire; now, if the discharge be effected by means of the discharger, between e_4 and i_1, four discharging currents will at the same time take place in the several wires, viz., one in the wire i_1 e_4 by means of a spark, and three without sparks in the uniting-wires e_1 i_2, e_2 i_3, and e_3 i_4.

If we term the quantity of electricity of the first internal coating *E*, and of the first external one *m E*, the second external coating, according to well known laws(2), will be charged with m^2E, the third with m^3E, &c. In short, the charges of the jars, following one another stepwise, are as $1 : m : m^2 : m^3$ &c., *m*, on account of the trifling distance between the coatings, representing a fraction which can differ but slightly from the unit.

For the purpose of measuring the effect of the discharges, Dove was the first to employ Riess's(3) improved electrical air-ther-

(1) Berl. Acad. Ber. 1847, 148, 237; Pogg. Ann. LXXII, 406.
(2) Biot, Traité de Phys. II, 407.
(3) Pogg. Ann. XL, 339.

mometer. When made part of the closing conductor between the internal coating i and the external e_1, e_2, e_3 and e_4 successively, the charges being the same for each, the rise of temperature caused by the discharges stood in the relation of the simple numbers 1, 2, 3, 4. Discharge by cascade.

If the thermometer was attached to the connecting-wire e_1 i_2, the temperature rose, on the discharge being successively effected by the closing conductors i_1 e_2, i_1 e_3, i_1 e_4. The elevation of temperature was the same for each of the connecting-wires, when the four jars were discharged by connecting i_1 and e_4, and nearly the same as that obtained in the closing conductor itself. When, therefore, the connecting-wires from one jar to another are equal, we obtain in all of them the same phenomena of heat, and the heat developed in each wire increases constantly in the ratio of the number of jars that are stepwise combined with one another.

If, after the charge is effected by cascade, all the internal and all the external coatings are put respectively in connection, the whole charge of the united internal surfaces will be $E\ (1+m+m^2+m^3)$, *i. e.* nearly 4 E, and of the external surfaces $m\ E\ (1+m+m^2+m^3)$, or nearly $4\ m\ E$. The relation of the two amounts of electricity $1 : m$ therefore remains the same as it was when each jar was considered by itself.

The elevation of temperature in the air-thermometer by the discharge of one jar being expressed by t, we must obtain nearly $4\,t$ by that of the entire battery of four jars; for the intensity of the electrical accumulation being the same, the elevation of temperature will be proportional to the quantity of electricity discharged(1). But the same elevation of temperature $4\,t$ was also obtained by the discharge by cascade between i_1 and e_4. Dove is of opinion, that this equality of effect whilst the quantities of electricity passing through the air-thermometer differ so much, can only originate in an inequality in the periods of discharge; since in the above-quoted valuable treatise of Riess on the rise of temperature produced in the closing conductor of the electrical battery, it has been proved that the rise of temperature due to equal quantities of electricity, is inversely proportional to the duration of the discharge(2). Consequently, if in the one case (the discharge by cascade) an amount of electricity = 1 passed through the thermometer in a unit of time, whilst in the other case a quadruple amount required a quadruple period, the heat produced in both cases must evidently be the same. The proof is now only

(1) Riess in Pogg.Ann. XL, 342. (2) Pogg. Ann. XLIII, 47.

Discharge by cascade.

wanting of the fact, that, when the discharge takes place stepwise, the duration of the discharge does actually diminish in the ratio here stated.

Dove has also examined the distance through which the discharge by cascade may be effected. The principal results of this investigation are exhibited in the following table of the calorific effects.

Closing conductors.	Ratio of electricities in the two surfaces.	Caloric effect.	Distance.
i_1 e_1	1 : m	t	x
i_1 e_2	1 : m_2	2 t	4 x
i_1 e_3	1 : m_3	3 t	9 x
i_1 e_4	1 : m_4	4 t	16 x

The discharging distance therefore increases in the ratio of the squares of the numbers of the jars disposed step-wise. This holds good whether the spark-micrometer be introduced in the external closing conductor, or in the connecting wires.

Electrical Currents produced by the Discharge of the Jar-battery.—The following papers on the effects of electric currents, produced by the discharge of the jar-battery, moreover, have appeared during the last two years.

K. W. Knochenhauer, on the ratio of tension in the electric lateral discharge. Pogg. Ann. LXX, 106, 255.

On phenomena connected with the electric charging current, by the same author. Pogg. Ann. LXXI, 343.

These papers are followed by others of the same author in Pogg. Ann. LXVI, LXVII, LXVIII, and LXIX. They do not permit of being given in abstract.

Development of Electricity by Steam.—There is a good historical essay by Mousson in Arch. Ph. Nat. IV. 5. intitled *Coup-d'œil historique sur le développement de l'électricité par la vapeur d'eau.*

Voltaic Combinations.—N. J. Callan, Professor of Physics in the Royal College of Maynooth, in Ireland, has attempted to substitute platinized lead(1) for the platinum in Grove's constant battery. It is not surprising that an arrangement of this kind, in which the lead is merely introduced as the conducting medium for the purpose of supporting a very thin lamina of platinum, should possess the same electro-motive power as Grove's battery, so long as the platinum-coating is sound, and we scarcely required experiments to prove the fact. It appears, however, that the platinized lead did not

(1) Phil. Mag. [3] XXXI, 81, Pogg. Ann. LXXII in abstr., 495; Arch. Ph. Nat. 1847, 47.

answer the expectations of Callan as to its durability under repeated use, as, according to a subsequent notice(1), he employs cast iron troughs for the reception of the nitric acid, or rather a mixture of nitric and concentrated sulphuric acids. He combined 577 elements with troughs of cast iron, and obtained, as may be supposed, extremely powerful effects. Poggendorff remarks, in reference to this apparatus, that although the cast iron is not likely to suffer much, so far as it is covered with the liquid, the parts external to the latter must very speedily be corroded by the nitrous acid fumes. Voltaic combinations.

Hence it follows, that neither platinized lead nor cast iron are adapted by their cheapness or actual utility to take the place of Bunsen's charcoal cylinders.

A real improvement in the constant battery which we owe to Callan, is however the addition, which he was the first to suggest, of concentrated sulphuric to the nitric acid; by this means, not only the conducting power is increased, but the action is maintained much longer uniform; in fact, it remains nearly so until the nitric acid is entirely consumed.

A powerful galvanic arrangement of platinum or copper with an amalgam of potassium has being described by Goodman(2). A glass tube, closed below with bladder, and containing petroleum, was immersed into a glass vessel partially filled with sulphate of copper, to which a little dilute sulphuric acid had been added. In the vessel was a strip of platinum, and the amalgam, attached to a copper wire, was immersed in the petroleum. As soon as the platinum was connected with one, the copper wire with the other platinum wire of a small decomposing cell, a vigorous and continuous decomposition of the water ensued.

Gas-Battery.—In 1842, Grove(3) described a species of voltaic combination, which he terms gas-battery, and which is essentially constituted as follows: glass tubes, open below and closed above, with strips of platinum fused therein, which previously had been platinized, *i. e.* covered with platinum-black(4), are partially filled in pairs (H and O) with hydrogen and oxygen respectively, and then each pair immersed in separate glass vessels containing acidulated water, in such a manner that the platinum of each tube is in contact with the dilute

(1) Phil. Mag. [3] XXXIII, 49; Pogg. Ann. LXXV, 128.
(2) Phil. Mag. [3] XXIII, 207; Arch. Ph. Nat. IX, 305.
(3) Phil. Mag. [3] XXI, 417; Pogg. Ann. LVIII, 202.
(4) The platinum-black, or extremely fine powder of that metal, is precipitated electrolytically upon the plates, from a diluted solution of bichloride of platinum. See Pogg. Ann. LXI, 593.

Gas-battery. acid. The platinum of the first hydrogen-tube (H_1) is in metallic connection with that of the second oxygen-tube (O_2), the platinum of the second hydrogen-tube (H_2) with the platinum of the third oxygen-tube (O_3), and so on, and, finally, the platinum of the last hydrogen-tube with the platinum of the first oxygen-tube (O_1). When the circuit is closed, a current is established in the direction from the hydrogen through the acid to the oxygen; it deflects the needle, decomposes water, and produces all the known effects of voltaic-electricity. The gases at the same time gradually disappear. If the battery is so contrived, that the quantity of the gases introduced and consumed can be measured(1), we observe that the ratio of the consumption of hydrogen and oxygen is, approximately, as 2 : 1. If a voltameter be introduced into the gas-battery circuit, we find that the volume of the gases evolved by the decomposition of the water is equal to the amount of gas disappearing simultaneously in each pair of tubes. Grove has undoubtedly drawn a correct conclusion from these facts, when he states the efficacy of the battery to be dependent upon the antagonism between these two gaseous bodies. For it is evident, that the strips of platinum of all the hydrogen-tubes, so far as they are moistened, and in the same manner those of all the oxygen-tubes, must suffer a change in the condition of their surfaces, similar to that of the battery-plates which are polarized with hydrogen and oxygen, and thus rendered heterogeneous. The current does, in fact, pass just as it does between two platinum plates placed opposite to one another in acidulated water and dissimilarly polarized; *i. e.* from the hydrogen, which represents the zinc of the ordinary combination, through the liquid, to the oxygen. The current continues because the oxidized hydrogen is constantly replaced by newly-dissolved hydrogen. The duration forms, in reality, the only essential difference between Grove's gas battery and Ritter's so-called charging pile(2) which is composed of polarized plates.

It is necessary, if we wish to obtain an effective gas-battery, to platinize the platinum strips, *i. e.* to invest them with platinum in a finely decided state; evidently because the spongy covering by its capillary action attracts the liquid into the gas-filled space, and thus multiplies the points of contact between the gases, the liquid, and the metal.

If the platinum strips are not in direct contact with the gases, *i. e.* if they are entirely immersed in the liquid, so that only those particles of gas which are held in solution by the latter, are in

(1) Pogg. Ann. Ergänz.-Bd. II, 369, from Phil. Trans. 1843, II, 91.
(2) Compare: Pogg. Ann. LXI, 599.

contact with them, the current does not actually cease altogether, but it is nevertheless very much weakened. Gas-battery.

When Grove, at starting, completely filled the oxygen-tubes of his battery with liquid, a current was perceptible, but one that was weaker than before. In this case, the deficient oxygen was gradually taken up from the atmosphere, for if the atmospheric oxygen was entirely excluded, the current ceased after a time. Grove then filled the oxygen-tubes with nitrogen; and the current was found to be constant, though the external atmosphere was entirely excluded. The nitrogen, in this case, merely served to afford the space, into which a little hydrogen was gradually introduced by diffusion. Consequently, at one platinum strip (the one surrounded by hydrogen) the hydrogen was oxidized, whilst at the other the same gas was evolved. This experiment, which at first sight appears rather startling, does not however differ essentially from the well-known fact, that a zinc plate forming a voltaic circuit with a plate of platinum in pure sulphate of zinc is oxidized, whilst metallic zinc is deposited upon the platinum.

Grove has also investigated the galvanic effects of other gases, when substituted in the glass tubes for oxygen and hydrogen. Effects similar to those just mentioned were, however, only observed when chlorine was substituted for oxygen, and carbonic oxide for hydrogen. The atmosphere being totally excluded, nitric oxide also, when opposed to oxygen, was found to produce a distinct effect, by assuming a higher state of oxidation(1). Even the vapours of some bodies caused electric currents, as, for instance, those given out by phosphorus at the ordinary temperature. For this purpose, a piece of phosphorus was introduced into one of the tubes, surrounded by some indifferent gas, such as nitrogen or carbonic acid, the opposite tube being filled with oxygen. The current was permanent, portions of the phosphorus being gradually oxidized. A piece of sulphur, treated in the same manner, produced no current; but, if heated to fusion, a deviation of the needle was at once observed.

Grove found that when atmospheric air was introduced into one of the tubes in the place of oxygen, hydrogen occupying the other it was gradually (*i. e.* after several days), and entirely, deprived of its oxygen, whilst the nitrogen remained unchanged in quantity or quality. In the same manner, a similar gas, containing hydrogen,

(1) Phil. Trans. 1845, II. Pogg. Ann. Ergänz.-Bd. II, 408.

Gas-battery.

lost every trace of hydrogen when opposed to oxygen(1). Grove, therefore, recommends the employment of one pair of the gas-battery as a safe, though slow resort, for eudiometric purposes, particularly when it is desirable to obtain very pure nitrogen, or to remove very small quantities of hydrogen or oxygen from a gaseous mixture. Poggendorff proposes a simpler process for the same purpose, though based upon the same principles.

Grove, as we have previously remarked, has attempted, and that by very sound arguments, to deduce the electromotive power of the gas-battery from the chemico-electrical antagonism of hydrogen and oxygen. Schönbein(2) of Basle does not, however, consider these arguments tenable, and accounts for the influence of the oxygen by its depolarizing power, a power analogous to that exerted by the nitric acid in Grove's constant battery. One would suppose that Schönbein had been led to this position by direct electromotive measurements, or that he had at least offered counter arguments of no less weight, in order to refute a series of logical conclusions; but he has done neither. His main objection consists in his own observation, that "an aqueous solution of oxygen being placed in voltaic connection with pure water," (how far deprived of air is not stated), "no current is produced, nor an effective voltaic pair formed, even though it be closed by platinum." Schönbein does not attempt to prove that platinum may not be negatively polarized by electrolysis; he merely adopts the view that the negative polarization does not depend upon the oxygen which is evolved at the platinum surface, but upon the ozone which is formed at the same time;—the all-interpreting famous ozone, Schönbein's hobby.—Grove had, however, expressly observed in his treatise, that the oxygen he employed was free from ozone. Nor does Schönbein ascribe the efficacy of the hydrogen in the gas-battery to the direct influence of this gas; he supposes that, under the influence of the platinum, a suboxide of hydrogen is formed from the hydrogen and water, and that this is the real cause of the positive polarity which the platinum attains in the atmosphere of hydrogen. Why, indeed, are we not to consider a solution of hydrogen in water as a suboxide of hydrogen?

Schönbein's observation, which we quoted in his own words, is, however, incorrect; it is refuted by numerous experiments, old as well as recent; by experiments which all tend to prove that the metals, from platinum to the easily oxidizable zinc, are polarized negatively

(1) Pogg. Ann. Ergänz.-Bd. II, 393. (2) Ibid. LXXI, 238.
(3) Ibid. LVIII, 361; LXXIV, 241.

by contact with oxygen, *i. e.*, that they are placed in a condition in which they appear to be shifted nearer towards the negative end of the series. Gas-battery.

We remind the reader, of the long known phenomenon, among others, that, of two pieces of the same metal successively dipped into a liquid, that which was first immersed, and from which, therefore, the atmospheric layer was first removed by the capillary action of the water, invariably behaves electro-positively to the other.

If a strip of platinum had, only for a moment, served as the positive pole of the weakest electric pile, even though no perceptible decomposition of water had taken place, it behaves as a more electro-negative metal to a second free piece of the same.—In the Edinb. New Phil. Journ., XXXVIII., Adie communicates an experiment, in which similar plates of zinc had been coupled voltaically with water; a current was at once produced if one plate was surrounded with dissolved oxygen. The plate placed in oxygen was invariably negative.

In all these, and in many similar cases, it cannot be doubted that an electro-motive action is exerted by oxygen, and that it is the only imaginable cause of the current. This influence of free oxygen is not as distinctly perceptible with heterogeneous metals when opposed to each other in the electrolyte. This question has lately been investigated by W. Beetz(1). He shows, that, if the liquid to be decomposed be water, the exclusion of air or oxygen on the side of the electro-negative metal, always causes a diminution of the initial force of the current, until a certain minimum is reached, and that the access of oxygen to the electro-negative metal at once elevates the force of the current, and even raises it above its original value. These experiments certainly prove that an essential part of the efficacy of free oxygen must have consisted in preserving the negative metallic plate in its original condition. Beetz, however, goes too far in his conclusions, when he absolutely excludes any simultaneous increase of the electro-motive power, as produced by the presence of oxygen. The solution of this question can only be attained by electro-motive measurements.

Passivity.—Various investigations have, of late years, been communicated on the subject of the passivity of iron, by W. Beetz(2), W. Rollemann, of Halle(3), and Gust. Wetzlar(4), who is well-

(1) Pogg. Ann. LXXIV, 381.
(2) Ibid. LXVII, 186.
(3) Ibid. LXXIII, 406.
(4) Ibid. LXXIII, 417.

Passivity. known to have been the first to describe this peculiar deportment, as early as 1827. All these papers essentially confirm the opinion as often adopted as rejected, that the passivity depends upon a thin film of oxide, with which the iron becomes coated under certain circumstances, and by which it is, on the one hand, deprived of part of its conducting power, and on the other withdrawn from the direct influence of nitric acid, and other oxidizing liquids.

It is evident that iron, invested with a coating of oxide, must exhibit a bearing similar to that of passive iron. But in what manner can we explain the origin of this protecting coat on polished iron, which, connected with platinum, and immersed in nitric acid, at once appears passive, and which, so long as it forms a galvanic chain with platinum, develops a constant, though weak current, being at the same time gradually, though very slowly, dissolved in the acid? Again, how is the oxide-coating compatible with the fact, that the passive condition obtained in nitric acid may be usually removed even by ablution in water?

Re-union of the Gases in the Voltameter.—Jacobi(1) has discovered that a gradual re-union of the gases, evolved in the voltameter, takes place even when the platinum electrodes are constantly covered with liquid, and are not, therefore, in direct contact with the gaseous mixture. Even when atmospheric air is present in the voltameter, their volume is said to be diminished under the influence of the platinum electrodes, though less rapidly than in the case of the undiluted explosive mixture.

Conduction-resistance.—Our knowlege of the doctrine of galvanic electricity has been much extended of late years by numerous, and, in part, very accurate measurements. The invention of constant batteries, the perfection of galvanic measuring instruments, the invention of the rheostat, which we owe to Wheatstone and Jacobi, have led to simplified modes of measurement, and have essentially contributed to the facility and certainty of the experiments, even when conducted by imperfectly practised hands.

The rheostat, which may be varied in its adaptation, according to the requirements of the case, consists, as is well known, chiefly of a mass of wire, which is introduced in the course of a galvanic circuit, and which, as often as necessary, may be rapidly elongated, shortened, or entirely excluded, without at all interrupting the current. If this regulator-wire is uniform throughout, the inserted length may at any

(1) Petersb. Acad. Bull. VII, 161; Ann. Chem. Phys. [3] XXV, 215; Pogg. Ann. LXX, 105; Compt. Rend. XXVII, 628; Instit. 1848, 398; Arch. Ph. Nat. X, 56.

time be easily and accurately measured, and we thus obtain a very simple means of calculating all the principal liquid and solid components of the circuit, as wire-lengths of the same kind, and consequently of reducing the entire conduction-resistance of the circuit to one length of regulator-wire. Conduction-resistance.

Let us suppose a conductor of unknown resistance inserted into a constant voltaic circuit, and then, the deflection of the galvanometer-needle having been observed, removed and replaced by the regulator-wire in such a manner that the deflection previously observed is exactly restored; the wire-length necessary to effect this, may serve as an expression of the resistance of that conductor. In this way, the regulator-wire may be employed as a common measure for comparing the resistance of the most various conductors.

This apparatus for determining the conduction-resistance is now frequently employed.

According to this method, Buff has measured the conduction-resistance of the following bodies:

Silver, chemically pure	1·000
Copper, „ „	1·048
Copper of commerce:	
First quality	1·227
Second quality	1·579
Nickel silver	12·401

The pure silver was prepared expressly for this purpose in the chemical laboratory at Giessen; the pure copper was very carefully prepared by the aid of galvanism, though not absolutely free from iron. Chemical analysis proved the presence of 0·02 per. cent. The first quality of the copper of commerce contained 0·22 per cent. of iron; the second, in addition to a trace of iron, 0·20 per cent. of lead, and 0·26 of nickel.

The transverse sections of the wires employed were all deduced from the weights of measured wire-lengths and their specific gravities.

Horsford, of Albany, (1) has adopted a method similar to the one just described, for measuring the conduction-resistance of some liquid bodies at a temperature of 18°—20° C. He employed a square trough of firm and compact wood for the reception of the liquids to be examined, 0·3 metres in length, 0·075 metres in breadth and in depth; internally it had a thick coating of shellac varnish, in order to

(1) Pogg. Ann. LXX, 238; Sill. Am. J. [2] V, 36.

Conduction-resistance.

prevent, or at least to impede as much as possible the absorption of the liquid. There were two pieces of board attached to the trough, of which one was fixed, the other moveable. They served to hold the plates immersed in the liquid, and to alter their distance at will. The plates, which were of the same size as the section of the box, were affixed to strips of copper, which again were screwed to the boards, and were in connection with a constant galvanic battery. The strength of the current was measured by means of a galvanometer introduced in the circuit.

The experiment was conducted so that two plates were placed exactly parallel to, and, at first, at a distance of 2·5 centimetres from, one another, in the trough, which was partially or entirely filled with liquid; the circuit was then closed, and the needle directed to a particular degree by means of a rheostat. The distance intervening between the plates was then increased by moving one of them, and the length of regulator-wire required to be withdrawn from the circuit, in order to restore the needle to its original position, was noted. It is evident that the increase of the layer of liquid effected as great a resistance as the wire unrolled, and that independently of the influence of polarization.

Horsford justified by his experiments the assumption not previously proved by direct observation, that the conduction-resistance of liquids is independent of the current-force, and that it is directly proportional to the length, and inversely proportional to the transverse section of the liquid mass.

The following are the numbers obtained by him for the conduction-resistance of chemically pure solutions.

Name and quality of liquid.	Conduction-resistance, that of pure silver = 1.
Sulphuric acid, sp. gr. 1·10	938500
" " " 1·15	840600
" " " 1·20	696700
" " " 1·24	696700
" " " 1·30	696700
" " " 1·40	1023400
Sol. of chloride sod. 27·6 grms. in 500 C. C. of water	7157000
" " 21·3	9542000
" " 10·65	18460000
" " 5·325	34110000
Sol. of chlor. potas. 27·7	7168000
Sol. sulphate of copper { 100 C. C. containing 15·093 grm. CuO, SO_3 }	12058000
The same quantity of the salt in a double volume of liquid	17490000
Sol. sulph. of zinc { 100 C. C. containing 7·287 grm. ZnO, SO_3, HO }	23515000

Conduction-resistance.

Edm. Becquerel has investigated the conductive power of solid and of liquid bodies, employing for this purpose a differential galvanometer(1); *i. e.* the current of a galvanic battery, split into two branches, was conducted into the latter so that they ran round the galvanometer-needle in opposite directions, and could consequently only affect it by the difference of their forces. The equilibrium of the two portions of the current could be restored by the resistance of a Wheatstone's rheostat, which was inserted into one of the branches; the needle could thus be retained in, or at all events be restored to, a quiescent position. This was done first with the instrument alone, and subsequently, after the substance to be examined in reference to its conducting power had been introduced into the other branch. The resistance of the latter was therefore directly compared with the resistance of a length of regulator-wire.

In this manner the following determinations have been performed for 12°—13° C.

	Conducting power for equal diameters after Annealing.	Ignition.
Silver, pure, reduced from the chloride	93·448	100·000
Copper precipitated electro-chemically, and fused	89·084	91·439
Gold, pure	64·385	65·458
Cadmium	24·574	—
Zinc	24·164	—
Tin	13·656	—
Palladium	13·977	—
Iron	12·124	—
Lead	8·245	=
Platinum	8·042	—
Mercury	1·8017	—

The mean diameters of the wires selected were measured under the microscope with the aid of a micrometer.

For the purpose of investigating the diminution of the conducting power at high temperatures, the wires, wound spirally, so that the separate turns of the coils could not come in direct contact with one another, were immersed in an oil-bath. E. Becquerel arrived at the conclusion that the diminution of the conducting-power is proportional to the increase of temperature. However, the results of his own experiments contradict this conclusion; nor is it compatible with the older, though very accurate measurements made by Lenz with electro-magnetic currents.

(1) Ann Ch. Phys. [3] XVII, 242; Pogg. Ann. LXX, 243 (in abstr.).

Conduction-resistance.

Some experiments have been conducted by J. Müller(1), of Halle, after a method similar to that employed by Becquerel, on the dependence upon temperature of the conduction-resistance of metals; he employed a very correct differential galvanometer constructed by Hankel(2). His measurements, however, were confined to iron, zinc and mercury, between the temperatures from 18° to 158° C. With regard to iron wire, he has arrived at almost the same results as those formerly obtained by Lenz; in the other two metals he does not find the resistance to increase in the ratio of the temperature, but the deviation is very trifling.

In order to ascertain the conducting power of liquids independently of polarization, E. Becquerel(3) inserted in each of the two branches of the divided current (see p. 221) a column of the same liquid, and re-established the equilibrium, first with this arrangement by itself, and subsequently, after a wire of known resistance had been introduced into one of the branches. The length by which the liquid column of the same branch required to be shortened, exhibited the resistance of the liquid.

The following are his results:

	Density.	Temp.	Conducting power.	Resistance.
Silver, pure, after ignition	—	0°·00	100000000	1
Water saturated with: Sulphate of copper	1·1707	9 ·25	5·42	18450000
Water saturated with: Chlor. of sodium at 9·5° C.	—	13 ·40	31·52	3173000
Water saturated with: Nitrate of copper	1·6008	13 ·00	8·995	11120000
Water saturated with: Sulphate of zinc	1·4410	14 ·40	5·77	17330000
250 grm. water with 30 grm. iodide of potassium	—	12 ·50	11·20	8928000
220 C.C. water and 20 C.C. sulphuric acid with 1 at. water	—	19 ·00	88·68	1128000
Nitric acid of commerce of 36° B.	—	13 ·10	93·77	1066000
20 grm. terchlor. of antimony, 120 C.C. water, and 100 C.C. hydrochlor. acid	—	15 ·00	112·01	892800

INFLUENCE OF THE DEGREE OF SATURATION.

	Amount of salt in equal volumes.	Power of conduction.	Resistance.
Sulphate of copper:			
Saturated solution	1	5·42	18450000
„ diluted to double vol.	½	3·47	28820000
„ „ quadruple „	¼	2·08	48080000
Chloride of sodium:			
Saturated solution	1	31·52	3173000
„ diluted to double vol.	½	23·08	4333000
„ „ treble „	⅓	17·48	5721000
„ „ quadruple „	¼	13·58	7864000

(1) Pogg. Ann. LXXIII, 434. (2) Ibid. LXIX, 256.
(3) Ann. Chem. Phys. [3] XVII, 267; Pogg. Ann. LXX, 250.

	Amount of salt in equal volumes.	Power of conduction.	Resistance.	Conduction-resistance
Nitrate of copper (density = 1·6008)	1	8·995	—	
„ „ diluted to $\frac{3}{2}$ volumes	$\frac{2}{3}$	16·208	—	
„ „ „ 2 „	$\frac{1}{2}$	17·073	—	
„ „ „ 4 „	$\frac{1}{4}$	13·442	—	
„ „ (density = 1·085)	—	8·979	—	

The conductive power of liquids varies with the temperature, but in a proportion inverse to that in metallic wires, *i. e.* it increases with the rise of temperature. The fact has been long known, but hitherto measurements were wanting. E. Becquerel(1) concludes from his experiments on this subject, which are not very numerous, that the increase of the conducting power proceeds proportionally to that of the temperature. This assumption must however be looked upon as a rude approximation to the truth. From a more detailed, though still unfinished investigation of Hankel(2), we learn that the conduction-resistance of liquids is very sensibly diminished by warming, but that this diminution is not proportional to the change of temperature, but is greater for a given difference of temperature, the nearer this approaches to zero. The various liquids appear to correspond tolerably in these variations, and only to differ from one another in this,—that those solutions, which contain a larger quantity of salts, suffer greater variation in their conducting power for the same differences of temperature. It is singular that the conductivity of a concentrated solution of sulphate of zinc, as well as of concentrated sulphuric acid, is increased by a moderate addition of water, but again reduced by greater dilution.

An investigation respecting the conduction-resistance in liquids has also been published by Marié-Davy(3), Professor of Physics at Montpellier. He conducts the electric current through a glass cylinder, filled with liquid, its bottom being closed by a suitable plate of metal. There was a second plate of the same horizontal section as the cylinder which could be moved up and down, and the distance between the two plates could be accurately measured. A coil of platinum was inserted in the same current, in such a manner that it could be easily excluded and replaced by a corresponding elongation of the liquid column. It is evident that in this manner the conduction-resistance of the liquid, quite independently of polarization, was reduced to that in the platinum coil. This is

(1) Loc. cit.
(2) Pogg. Ann. LXIX, 258; Arch. Ph. Nat. IV, 66.
(3) Ann. Ch. Phys. [3] XIX, 401.

Conduction-resistance. essentially the same method as that employed by Horsman, and several years ago recommended by Wheatstone(1).

Marié-Davy has not arrived at any new facts.

Dr. Smaasen, of Utrecht, has published an analytical investigation of the dynamic equilibrium of electricity in a body and in unlimited space; from which, among other results, it would appear that the electrical conduction-resistance of the earth is equal to that of a cylinder of the same material as the earth, whose length is equal to a semi-radius of the electrodes (supposing them spherical), sunk into the earth, its transverse section being equal to a great circle of these electrodes. We must refer to the treatise itself for the details(2).

Influence of Atmospheric Electricity upon Telegraphic Conductors.—It is well known, that the wires of the electric telegraph laid down at Göttingen by Gauss and Weber, were several years ago fused by a stroke of lightning. Since that time, the effect produced by atmospheric electricity, and especially by electric clouds, upon copper wires supported in the air, has been frequently observed. At various places the electricity of the clouds has, during the discharge of a thunder-storm, been propagated through large distances by the wires; indeed, the telegraphic needles have repeatedly been set in motion. Accounts of these occurrences are to be found in the publications cited below(3).

Polarization.—One of the chief difficulties with which physicists had to deal in galvano-electric measurements, previously to the invention of the constant battery, was the great variation in the strength of the currents, which was attributed to a peculiar condition of the surfaces of the immersed plates, caused by the current itself, termed *polarization*. Subsequently, several physicists adopted Fechner's assumption of a special *transition-resistance*, to which the current was liable while passing from solid to liquid conductors, and *vice versâ*; whilst others, headed by Ohm, attempted to demonstrate, that the fact of galvanic polarization sufficed of itself for the explanation of all the phenomena connected with this resistance. The latter view appeared the more probable, the more the true nature of polarization was elucidated. It has been found, that it is invariably caused by the deposition of foreign matter on the surface of the plates; it is evident that such a deposition must in every case be the immediate and necessary con-

(1) Pogg. Ann. LXII, 530. (2) Ibid. LXXII, 435.

(3) Compt. Rend. XXIII, 546; XXIV, 980; Phil. Mag. [3] XXX, 186; Arch. Ph. Nat. IV, 298; Pogg. Ann. LXXI, 358; LXXIII, 609; LXXVI, 135.

sequence of the current, and of the decomposition of the liquid, and that by a removal of this foreign matter the original force of the current could always be restored. Polarization.

A platinum-plate, for instance, surrounded by sulphate of copper, and forming the negative member of a galvanic arrangement, begins to be covered with metallic copper as soon as the current passes; when immersed in sulphate of zinc it becomes gradually coated with zinc. In reference to its electric deportment, it must, therefore, in the former instance, approach more and more to that of a plate of copper, in the second to that of a zinc plate, *i. e.* the motive power of the current must be diminished.

If dilute sulphuric acid, or an alkaline solution, be decomposed in a galvanic circuit, the negative pole-plate becomes enveloped with hydrogen, as, in the previous cases, with copper or zinc; the electro-positive plate, unless dissolved in the liquid, causes the evolution of, and is covered with oxygen. Now oxygen forms the electro-negative termination of the tension-series. Hydrogen, on the positive side, certainly stands superior to zinc(1). Could we assume, that these gaseous deposits accumulated to such density as to prevent the immediate contact between the metallic surface and the liquid, we should no longer have two metallic plates, but, as it were, a plate of oxygen and one of hydrogen opposed to one another in this medium. It is evident that this would give rise to an electro-motive power in a direction contrary to the original one, and of much greater intensity than that of the copper-zinc, or even of the carbon-zinc pile. The electro-excitant power of hydrogen with oxygen therefore indicates the limits of the intensity attainable by polarization, —a limit, however, which is probably never reached even under the most favourable circumstances.

In the ordinary (inconstant) zinc-copper or zinc-platinum battery, which is closed by dilute sulphuric acid, only the electro-negative metal is polarized, and that by hydrogen. The hydrogen is positive as regards the zinc; therefore, a hydrogen-coating of sufficient density must cause the current to be reversed. A polarization of such intensity cannot however occur under ordinary circumstances, because the secondary electro-motive power cannot possibly become greater than the primary one by which it is called into existence. In a pile formed with zinc and any more electro-negative metal, the current will therefore always pass from the zinc through the liquid to the other metal; but it is evident, that, as long as the current and

(1) Ann. Ch. Pharm. XLI, 136.

Polarization. the decomposition continue, the polarization must increase until, the force of the current constantly diminishing, the residual decomposition establishes an equilibrium with that quantity of gas which is continually being removed from the metallic plate, either by its expansive property, or by the solvent power of the liquid.

It may consequently be anticipated that the polarization induced in the circuit of a battery, by hydrogen, or by hydrogen and oxygen, must increase in the ratio of the electro-motive power of the series; but only until the above-mentioned limit has been actually or nearly attained.

Wheatstone was the first, if not to recognise the resistance of polarization as an electro-motive counter-force, at least to introduce it into Ohm's formula, which thus assumed the following form(1),—

$$Q = \frac{n K - p}{n R + r}$$

The magnitude and influence of this counter-force, in various relations, has been more closely defined by various physicists(2). All the investigations that have been published agree in stating that the polarization of the platinum plates, resulting from hydrogen and oxygen, assumes, whenever an active decomposition of water has commenced, a value which is almost invariable, or, more correctly, which increases almost imperceptibly with the strength of the current. The distance between the plates, their size, and the depth of immersion have no influence, provided there be an active development of gas at all points. In weaker currents, however, which are accompanied by an imperceptible, or but very trifling decomposition of water, the polarization increases with the force of the current.

The numerical value of polarization at its maximum (for platinum plates in dilute sulphuric acid), exceeds by 1½ times the force of a constant carbon-zinc or platinum-zinc element, and, therefore, almost attains three times the force of a constant copper-zinc pair. Accordingly, it is perfectly intelligible that, in order to obtain an effective decomposition of water in a decomposing cell with platinum plates, not less than two carbon-zinc elements, and not less than three copper-zinc elements can be employed. If,

(1) Phil. Trans. 1843; Pogg. Ann. LXII, 533.

(2) Daniell in Phil. Trans. 1842, and Pogg. Ann. LX, 387; Lenz in Pogg. Ann. LIX, 226, 407; Lenz and Saweljew in Ann. Ch. Phys. [3] XX, 184; Poggendorff in Pogg. Ann. LXI, 606; LXVII, 528; (also Ann. Ch. Phys. [3] XX, 217); Pogg. Ann. LXX, 178; Svanberg in Pogg. Ann. LXXIII, 298; Buff in Ann. Ch. Pharm. XLV, 137; Pogg. Ann. LXXIII, 497.

however, the decomposing cell consists of two parts, separated by a porous partition, the one being filled with solution of caustic potassa, the other with dilute sulphuric acid, and if this voltametric apparatus be so connected with the galvanic arrangement, that the oxygen must be developed at the platinum plate which dips into the potassa, the hydrogen at the platinum plate in the acid, Poggendorff states that a powerful decomposition is effected by *one* of Grove's, or even one of Daniell's pairs(1). Polarization.

Poggendorff has made the remarkable observation that platinized platinum plates are subject to a much lower degree of polarization in a decomposing cell filled with dilute sulphuric acid, than platinum plates in the ordinary polished condition. Accurate measurement yielded the following results(2) :—

1st. The maximum polarization with platinized plates is about one quarter of its value less than with polished plates, and consequently but slightly exceeds the power of a single Grove's cell.

2nd. The polarization of platinized plates varies less with the variations of the force of the current than it does in polished plates.

3rd. In the former it attains its maximum more rapidly than is commonly the case in the latter, unless they possess a high degree of polish.

Poggendorff's attention was drawn to this deportment of platinized plates by the fact, that when connected as electrodes with a single Grove's pair, they yielded a considerably greater quantity of gas than did polished plates. De la Rive had noticed the same phenomenon as early as 1843.

Nor is polarization equally intense, under an equal strength of current, with different liquids, which yield oxygen and hydrogen by electrolysis. Thus solutions of pure potassa, or of sulphate of soda, effect a resistance which is to that of dilute sulphuric acid, as 120 : 100. The degree of concentration is of no consequence.

The polarization decreases as the temperature of the decomposing liquid rises, as Poggendorff first noticed, and as Dr. E. Becker, of Giessen, has proved, in a yet unpublished investigation, by accurate measurements.

It has been found that the polarization is liable to more or less

(1) Berl. Acad. Ber. 1847, 440; also Pogg. Ann. LXXI, 132, in Arch. Ph. Nat. V, 278 (in abstr.).

(2) Pogg. Ann. LXX, 186; extr. in Arch. Ph. Nat. V, 163.

(3) Archives d'Électricité, III, 159.

Polarization. perceptible variations, according to the nature of the immersed metal. Taking platinum always as the positive decomposing plate, the negative one being alternately silver, copper, or some other metal which lies nearer to the negative end of the tension-series, so long as the process of decomposition proceeds actively, no considerable difference in the intensity of the counter-force is perceived [Svanberg(1)], although a distinct increase from the platinum to the silver, to the copper, &c. is visible. The difference becomes, however, very perceptible when electro-positive metals are employed. If, for instance, the hydrogen was developed on an amalgamated strip of zinc instead of on platinum, the counter-force (which, in this case, is compounded of the electro-motive relation of the hydrogen to the zinc, and of the zinc to the platinum), attained a value which was greater by almost one half(2).

This difference would not exist, and the chemical character of the metal immersed would be quite immaterial, if the strip which is immersed could be entirely isolated from the liquid by the hydrogen which surrounds it. Now, as this is not the case, it follows necessarily, as demonstrated by experiment, that polarization generally attains a higher value in liquids which are more or less mixed with metallic solutions, than in chemically pure dilute sulphuric acid.

A. Saweljew(3) has observed that platinum plates which had served as poles of an electric pile, and had thus been polarized, even after they had apparently become quite homogeneous again, still preserve an heterogeneous relation to magneto-electric currents; *i. e.* that they impair or enhance the development of these currents according to their direction.

The recent labours of German and English physicists on the nature, influence, and extent of polarization, appear to have been as yet little noticed in France. Marié-Davy, in two very discursive treatises,—*Recherches expérimentales sur l'électricité voltaique*(4),—speaks of transition-resistance and polarization as of two essentially different things, and gives numerical values for both. In the course of his investigations, he arrives at the result that Ohm's law is incorrect, and he tries to rectify its incorrectness. Marié-Davy does not appear to have thought it possible that the error might be

(1) Pogg. Ann. LXXIII, 305; Arch. Ph. Nat. IV, 296.
(2) Pogg. Ann. LXXIII, 504.
(3) Ibid. LXXIII, 516.
(1) Ann. Ch. Phys. [3] XIX, 401, 422; XXII, 257; Arch. Phys. Nat. VII, 303 (in abstr.).

owing to his own mode of viewing the question, and to the inaccuracy of his experiments, for the correctness of which the reader has no control whatever. Polarization.

The younger Becquerel(1) has also worked, and it would appear to more purpose, at the same subject. There is, however, nothing really new in this part of his treatise.

Electro-motive Power.—A. F. Svanberg(2) has investigated the influence which the quality, and more particularly the degree of concentration, of the solutions, into which the plates are dipped, exerts upon the electro-motive power of Daniell's battery. The state of concentration appeared to have no influence in the case of a solution of sulphate of copper. This, however, is probably only true for the development of weak currents, as the copper plate is partially polarized by hydrogen under powerful currents in a dilute solution of copper. If the unamalgamated zinc plate was first placed in a concentrated, and then successively in more and more dilute solutions of sulphate of zinc, the power gradually rose in the proportion of 15·6 to 16·15. Dilute sulphuric acid employed in the place of sulphate of zinc, caused a reduction of the force to 14·14. If concentrated sulphate of soda solution was employed, the force was gradually elevated to 16·57, and was but slightly diminished when this liquid was diluted. The strength of the current from which the electro-motive power was derived remained the same in all the experiments.

It is remarkable, that the above-mentioned irregularities disappear entirely, or almost entirely, when the zinc is employed in the amalgamated condition. Svanberg attributes this to a polarization of the amalgamated zinc plate, effected by hydrogen, under the influence of the mercury. But if the hydrogen exerted any influence, this would be more perceptible in the non-amalgamated plates; the latter, however, present exactly the converse deportment, being electro-negative to the former. This electro-negative condition is well-known to be most marked in corroded and impure plates of zinc; this may account for the fact, that non-amalgamated plates presented a lower electro-motive power in dilute sulphuric acid, in which they were at once violently attacked, than in a solution of sulphate of zinc,—with more probability than can any difference in the effect of contact of various liquids upon the zinc. For various series of observations, communicated by Buff(3), prove, that, as often, at least,

(1) Ann. Ch. Phys. [3] XX, 62; Compt. Rend. XXIV, 376 (in abstr.); Arch. Phys. Nat. IV, 300.
(2) Pogg. Ann. LXXIII, 291. (3) Ibid. 507.

Electro-motive power.

as powerful currents are set in motion, the liquid conductors within the circuit, whilst they are decomposed by the current, are unable to contribute anything, either negatively or positively, to the value of the electro-motive power, by their contact-effect upon the surface of the immersed solid conductors.

If a vessel be divided into two cells by a porous partition, and the one filled with sulphuric acid, the other with sulphate of copper, and two connected strips of copper dipped into them, it is known that a weak though permanent current will be produced. If we now conduct through such a pair, or even through a series of such pairs, the much stronger current of a single Bunsen's cell, whose electro-motive power had been previously determined, we do not discover in this compound battery the slightest addition to the motive power. Owing to the increased oxidation, and consequent impurity of the copper immersed in the sulphuric acid, even a slight diminution was noticed; this, however, did not amount to one per cent of the electro-motive power of the carbon-zinc pair, when three such pairs of copper strips were placed in series.

Amalgamated zinc plates presented a similar behaviour, when immersed in sulphate of zinc solution, and in sulpuric acid. In consequence of the oxidation of one zinc plate whilst the surface of the other still remained uncorroded, a slight increase in the electro-motive power was observed. Sulphuric acid, and solutions of sulphate of copper and of sulphate of zinc, are the liquids that are present in Daniell's battery. In the above facts, then, we have a proof that the power of this battery depends essentially upon the electric difference between the metallic copper and zinc alone, and is not augmented by any electromotive effect of the liquids upon the metallic surfaces.

If the power of the constant carbon-zinc battery, when common nitric acid is employed, be termed 7·16, that of Daniell's arrangement is 4·207. If the sulphate of copper solution was replaced by fuming nitric acid, which is known not to affect copper, 4·324 was obtained. The presence, therefore, of nitric acid, when strong currents are passing, though it excites copper electro-positively with so much power, has but a very slight influence in increasing the electro-motive power; and even this would appear to be unconnected with the electro-motive power of nitric acid; for other variations also in the fundamental experiment(1) indicated the force 4·3 and con-

(1) Pogg. Ann. LXX, 62.

firmed the fact, that sulphuric acid, and solution of sulphate of zinc, in which a copper-zinc pair are immersed, do not contribute perceptibly to its electro-motive power. Electro-motive power

The power of copper (in dilute sulphuric acid), in relation to platinum (in fuming nitric acid), was found = 2·995. The power of copper to zinc, 4·3, added to this, yields 7·395. The power of zinc to platinum, in fuming nitric acid, measured directly, was = 7·375. The power of zinc to carbon, in fuming nitric acid, = 7·856.

The polarization of zinc by hydrogen was found nearly = 0·9. Consequently the electro-motive power of a strip of zinc, closely surrounded by hydrogen, to platinum is 7·375 + 0·9 = 8·275. If oxygen was developed at the platinum pole, and hydrogen at the zinc pole, the number 16·90 was obtained as the relative value of polarization. The polarization of platinum by oxygen, therefore, corresponds to the number 16·90 — 8·275 = 8·625. Poggendorff formerly obtained very nearly the same result.

We know from electroscopic and galvanometric experiments, that dissimilar liquids exert an electro-motive power at their surface of contact. It was therefore to be assumed that metallic sulphates would exert a similar effect upon sulphuric and nitric acids, and the two acids upon each other. This influence however, if it exist at all, can be but very trifling, for it was impossible to measure it with any degree of accuracy. On the other hand, a comparatively strong electro-motive power is observed at the contact-surface of nitric acid and potassa; to determine its amount, a glass vessel was partially filled with fuming nitric acid; a cell of porous clay, containing caustic potassa, was placed in it, and a carbon-cylinder introduced into both liquids. When the circuit was closed, the oxygen developed at the positive pole, by the simultaneous influence of the carbon and potassa, was at once employed in the formation of carbonate of potassa, whilst the hydrogen deposited at the negative pole was oxidized into water by the nitric acid. No resistance could therefore be produced by polarization. The electro-motive power of this circuit was 3·59.

The determination of electro-motive forces from the strength of the current upon the basis of Ohm's law admits of extreme accuracy, though only available for constant batteries. Some time ago, Poggendorff suggested a very ingenious method for the purpose of measuring the force of inconstant, with the same correctness as that of constant arrangements. It depends essentially upon preventing the current of the inconstant chain from coming into

Electro-motive power.

action, by employing the force of a constant element of known value(1). This proceeding, termed by Poggendorff the *method of compensation*, notwithstanding its advantages, has not so far as we know, been hitherto employed by other physicists; the following details may therefore be acceptable.

If the electro-motive powers of a constant pair, *e.g.* one of Grove's (I), and a variable one *e.g.* a copper-zinc pair (II) in sulphuric acid, are to be compared, the plates of the former are to be directly united by means of a wire *a*; a second wire *b*, which includes a delicate galvanometer, is made to proceed from the platinum plate of pair I, to the copper plate of pair II., and lastly the two zinc plates are placed in metallic connection. It is evident that the current of the constant pair is divided at the point of union of the wires *a* and *b*, and tends to circulate in part directly through the wire *a*, and in part through the wire *b*, and through the connections of the element II, to the zinc plate I. In the same manner the current that may be developed by the inconstant pair, will be divided, and after passing through wire *b*, it will tend, at the point of union of the wires *b* and *a*, return to its source partly through *a*, and partly through the connections of element I. We will now examine each of these currents separately. Let Q' and Q'' represent their forces when freely developed, and K' and K'' their electromotive powers. Let r be the conduction-resistance of the wire *a*, expressed in coils of the regulator; r' the resistance of the remaining portion of the constant cell, considered as directly closed by the wire *a*; r'' the reduced resistance of the inconstant cell, inclusive of that of the wire *b*.

The reduced conduction-resistance of the two branches of the current Q', viz. of the wire-lengths r and r'' being termed R', then the transverse section, referred to the length-unit selected (one turn of the regulator), is $\frac{1}{R'} = \frac{1}{r} + \frac{1}{r''}$, therefore $R' = \frac{r\,r''}{r+r'}$; the entire resistance of circuit I,

$$R' + r' = \frac{rr' + rr'' + r'\,r''}{r + r''};$$

and the force of the current,

$$Q' = \frac{K'\,(r + r''}{rr' + rr' + r\,r''}.$$

(1) Pogg. Ann. LIV. 172.

Then, if the reduced conduction-resistance of the two ramifications r and r' of the current Q'' be termed R'', we get $\frac{1}{R''} = \frac{1}{r} + \frac{1}{r'}$, Electro-motive power.

therefore $R'' = \frac{r\,r'}{r + r'}$; the entire resistance of circuit II,

$$R'' + r = \frac{rr' + rr'' + r'\,r''}{r + r'};$$

and the force of the current,

$$Q'' = \frac{K''\,(r + r')}{rr' + rr'' + r'\,r'}.$$

Let the portions of the current Q' traversing the ramifications r and r'' be termed q and q''; according to Ohm's law then we have $Q' : q :: \frac{1}{R'} : \frac{1}{r}$ and $Q' : q'' :: \frac{1}{R'} : \frac{1}{r''}$; hence

$$q = Q'\,\frac{R'}{r}, \text{ and } q'' = Q'\,\frac{R'}{r''}.$$

But the entire current Q'' tends to take its course, in opposition to the branch-current q'', through the ramification r'', *i. e.*, through the connections of the pair II, and through the wire b. The current that actually passes through the wire b is therefore,

$$q'' - Q'' = Q'\,\frac{R'}{r''} - Q'' = \frac{K'\,r - K''\,(r + r')}{rr' + rr'' + r'\,r''}.$$

If a rheostat be included in the wire a, we may, by a suitable elongation or reduction of this wire, make $q'' = Q''$; therefore $K'\,r = K''\,(r + r)$ and

$$K'' = \frac{K'\,r}{r + r'} \quad (a).$$

In this case no current passes through the wire b, the electromotive power K'' is not developed, and the only exit for the current produced by the power K' is the wire a. Consequently

$$Q' = q = \frac{K'}{r' + r}, \text{ and } K' = q\,(r' + r)$$

If we introduce this value of K$'$ in the equation (a), we obtain

$$K'' = q\,r \quad (\beta)$$

If, therefore, we know the conduction-resistance r, and if a sine- or tangent-needle be introduced in the wire, a, for the purpose of measuring the current-force q, the required force K'' results directly from the equation (β).

Electro-motive power.

When the experiment is made, attention should be particularly directed to maintaining the index, of the galvanometer included in wire *b*, permanently at zero, and this even during the repeated opening and closing of the circuit. If this precaution be neglected the value of K'' will be impaired by polarization.

Poggendorff formerly proved the practicability of the method of compensation by several experiments. He has recently reverted to the subject, and while testing it by numerous comparative experiments, he has developed all the requisites for a practical application of his method(1). He has also employed this process for the purpose of testing the correctness of the law of Volta's tension-series. For this purpose, strips or bars of three different metals were simultaneously immersed in a vessel filled with liquid, and alternately examined in pairs as to their electro-motive power. Very different metals were, in this manner, subjected to examination in various liquids, and every possible precaution required in such delicate investigations, observed.

As the method of examination is based upon the non-completion of the current, we should have been led to expect that the electro-motive influence of one liquid would have differed for each of the three metals. This, however, was not the case, at least, not so as to interfere with the general validity of the law, for, although the absolute values of the electro-motive forces varied in a marked manner in the different liquids, still Volta's law was fully confirmed; *i. e.* for any three metals, *a*, *b* and *c*, taken at random from the series, the sum of the electro-motive forces of *a b* and *b c* was equal to that of *a c*. For instance, taking the electro-motive power of amalgamated zinc to copper (both in dilute nitric acid) at 16·61, that of copper to platinum was found equal to 11·60, of zinc to platinum at 28·18.

For the three following purely theoretical papers of G. Kirchhoff, as they are not suited for abstraction, we must refer the reader to the original sources.

1. On the passage of an electric current through a plane, and especially through a circular plane(2).

2. On the solution of those equations, to which we are conducted by the examination of the linear distribution of galvanic currents(3).

3. On the applicability of the formulæ for the intensities of

(1) Berl. Acad. Ber. 1846, July; Pogg. Ann. LXX, 60 (in abstr.); Arch. Ph. Nat IV, 399.

(2) Pogg. Ann. LXIV, 497.

(3) Ibid. LXXII, 497.

galvanic currents in a system of linear conductors to systems which consist, in part, of non-linear conductors(1). Electro-motive power.

Development of Heat in Current-Conductors.—It is known that every portion of a closed circuit of conductors, traversed by the electric current, developes an amount of heat proportional to the square of the force of the current, and to the reduced length of the conductor involved. This theorem was first established by P. Riess(2), for the discharges of the electricity accumulated in the Leyden jar. Its correctness, as applied to galvanic currents, was therefore probable; this was not exhibited experimentally, however, till some years later, viz., by Joule(3), by measurements of temperature for wires and for liquids, by E. Becquerel for liquids(4), and by Lenz(5) by very careful measurements for metallic wires.

Now as this law has equal value for every conductor enclosed in the circuit, whether solid or liquid, it is to be expected, that it is also correct for the sum of all conductors forming the circuit, *i. e.* for the circuit itself. By arriving at this conclusion Poggendorff(6), was conducted to the following corollaries:

Let r represent the reduced conduction-resistance of the entire pile, q the current-force, then the entire amount of caloric developed in the unit of time is expressed by the equation, $w = q^2 r$. If this expression be combined with the well known formula of Ohm, $q = \frac{K}{r}$ we obtain $w = q\,K$, or $w = \frac{K^2}{r}$. The first equation shows, that, for a given electro-motive power, the amount of heat is augmented and diminished in the ratio of the current-force, or of the quantity of zinc dissolved; but that for a given current-force the amount of heat is in the ratio of the electro-motive power; that for instance, more heat is developed by a Grove's pair, with equal current-force, in the entire extent of the closed circuit, than by one of Daniell's, since the reduced wire-length r, is smaller in the latter.

It also results from the second equation, that, by the diminution of the conduction-resistance, the electro-motive power being unaltered, the total development of heat, as well as the force of the current itself, may be increased *ad infinitum*.

Poggendorff has proved the correctness of these theoretical

(1) Pogg. Ann. LXXV, 189.
(2) Ibid. XL, 335; XLIII, 47; XLV, 1.
(3) Phil. Mag. [3] XIX, 260.
(4) Ann. Ch. Phys. [3] IX, 21.
(5) Pogg. Ann. LXI, 18.
(6) Berl. Acad. Ber. 1847, 410; Pogg. Ann. LXXIII, 337; Arch. Ph. Nat. VIII, 204 (in abstr.); Instit. 1848, 191.

Development of heat in current-conductors.

considerations by a few well chosen experiments(1). In order to measure the quantity of caloric produced by the current in a metallic wire, Poggendorff recommends an instrument constructed as follows:—A spiral coil of thin platinum wire is placed in a thermometer-shaped bulb filled with alcohol, passing through the glass at two opposite points; its reduced resistance to conduction having been ascertained, a current is passed through it. The heat produced passes into the liquid, and causes a corresponding elongation of the column of it in the thermometer-tube. Poggendorff calls this apparatus, which appears peculiarly adapted to the study of the calorific effect of the current in metallic wires, a galvano-thermometer(2).

Hankel(3) has made some experiments in order to deduce the the force of electric currents from the elongation due to heat, which takes place in a wire traversed by the current. It is, however, impossible to explain the instrument designed by him for this purpose without the aid of a drawing. The experiments which he has communicated evince its utility; and it also appears to possess real advantages over the ordinary galvanometers in some cases, and especially for the measurement of those currents, which, like the magneto-electric currents, vary in their direction.

E. Becquerel(4) has repeated the well-known experiments of Peltier on the production of heat or cold at the points of contact of two different metals, through which the current passes, with a view to ascertain the influence which this deportment exerts upon the resistance to conduction developed during the passage of the current from one conductor to another. He was not however able to discover any influence of the kind.

Tyrtov has noticed, that if mercury be employed as the electrodes of Daniells' battery, and the circuit be closed with a metallic conductor, so that one of its ends is immersed in the mercury of the positive, and the other is merely in contact with the negative pole, the latter end becomes red-hot and melts. If the proceeding be reversed, a mere blueish spark is perceived at the end of the wire, whilst the mercury is more heated than before, and evaporates(5).

The similarity of this deportment to the well-known older observation of Neeff(6) is at once apparent. Tyrtov did not however succeed in producing the same phenomenon if he employed another metal

(1) Pogg. Ann. LXXIII, 343.
(2) Ibid. LXXIII, 361.
(3) Ibid. LXXV, 206.
(4) Ann. Ch. Phys. [3] XX, 55.
(5) Pogg. Ann. LXX, 85, from Petersb. Acad. Bull. V, 94.
(6) Pogg. Ann. LXVI, 414.

Development of heat in current conductors.

in the place of mercury. Neeff(1) observes in reference to this point that "the success of the experiment depends upon the discharging-contact being as brief as possible, for the negative wire also rapidly becomes hot, because, as a conductor, it is indifferent to the poles, and conducts the heat of the positive pole with which it is in contact. It is also requisite that the thickness of the wire be in due proportion to the strength of the battery; it should not be too thick. The experiment is rendered most convincing, if a wire be connected with each of the poles, and if each of these wires be taken between two fingers, and one of them be struck rapidly and repeatedly against the other; it is still better to notch one wire like a saw and to pass the other perpendicularly over it, repeating this movement often and rapidly." The first observation on the difference in the origin of electric heat and light is well known to have been made by Neeff, by means of the current-breaker, described in 1839(2). This ingenious and well-known apparatus, which has been most usefully employed in the electric telegraph, was re-invented by M. Froment, in Paris, in 1847(3).

The Luminous Arc.—The two terminal points of a galvanic battery of considerable electro-motive power, once brought into contact, so that the current may pass, may, as is well known, be more or less separated without interrupting the current, the maximum distance of separation of course varies according to the power of the battery, but, under the influence of very powerful piles, it may be even increased to several inches. In that case a luminous arc extends between the two poles, and a transference of incandescent particles from one to the other may be perceived. It is this transition of finely divided matter which serves as a conductor to the current and preserves its continuity. The length of the luminous arc consequently bears a close relation to the facility with which the material of the poles admits of division [De la Rive(4)]. Physicists have hitherto very generally adopted the opinion that the transference of material particles which attends the luminous arc, proceeds only from the positive to the negative pole; and the above-mentioned discovery of Neeff, that the positive is more strongly heated than the negative pole, appeared to present the key to the solution of this problem.

Recent experiments by Van Breda, of Haarlem(5), represent the

(1) Pogg. Ann. LXIX, 142. (2) Ibid. XLVI, 104.
(3) Compt. Rend. XXIV, 428; Arch. Ph. Nat. IV, 294.
(4) Pogg. Ann. LXXVI, 275.
(5) Compt. Rend. XXIII, 462; Pogg. Ann. LXX, 326; Arch. Ph. Nat. III, 32.

The luminous arc. matter differently, viz. that incandescent and fused particles are not only propelled from both poles towards one another, but in every direction. Van Breda has, in various cases, determined the amount by weight of the quantity of matter carried off at both ends, but he does not decide whether it is in excess at the positive pole.

According also to the observations of Maas, of Namur, the mechanical transference of ponderable matter is not always directed from the positive to the negative pole; he considers the quality of the electrodes to be the efficient cause of the direction of the transference. He succeeded in preparing two charcoal cylinders in such a manner that the grain of the one was finer and harder than that of the other. If the positive pole was connected with that of finer, the negative with that of coarser grain, and both pointed near their ends, a movement of incandescent particles was effected from the negative to the positive pole, as soon as the luminous arc was formed. The negative cylinder afterwards appeared slightly excavated, the positive one only slightly obtuse(1). It is rather surprising, that the author has not examined the influence of a reversion of the current.

Van Breda has employed an ingenious method for producing the arc of light, without previously bringing the two poles into contact. He did this by causing the spark of a Leyden jar to be discharged between them; in reference to which Poggendorff observes, that the same artifice had been previosuly employed by J. Herschel and by Sturgeon. De la Rive states Daniell to be the inventor of this proceeding. It depends upon the circumstance of the discharge being always combined with a transference of substance in extremely minute subdivision, which closes the circuit during the time necessary for the formation of the arc(2).

The difference, between the results obtained by Van Breda and those of other observers, may be caused by his having allowed the electric current to continue too long, (see above,) so that the incandescent state of the anode was communicated to the cathode; for de la Rive has also confirmed the fact of the transference of the particles proceeding mainly from the positive pole, and that, when the luminous arc was formed between two similar metallic wires, *e. g.* between platinum or silver wires, the positive wire was always first rendered incandescent(3).

On de la Rive's employing a platinum plate as the positive pole,

(1) Instit. 1849, 46; Arch. Ph. Nat. X, 227.
(2) Pogg. Ann. LXXVI, 273.
(3) Phil. Trans. 1847, 1 Pogg. Ann. LXXVI, 270; Arch. Ph. Nat. IV, 350.

and placing opposite to it a platinum point as the negative pole, and then producing the luminous arc, a circular blue spot was formed on the platinum resembling the coloured rings of Nobili. De la Rive considers it as the result of an oxidation of the platinum, (it is not stated whether his platinum was free from all foreign admixture,) because it was not produced in an atmosphere of hydrogen. On reversing the experiment, the platinum plate was covered all round the opposed platinum point with innumerable small platinum globules, which, when examined by the naked eye, formed a white spot. If the experiment was continued for some length of time, (1 to 2 minutes,) the point was fused. On the other hand, if the wire formed the negative pole, as above, it certainly was heated, but without fusing; but the plate, when not very thick, was easily perforated. The luminous arc.

De la Rive(1) has observed a singular influence of magnetism upon the voltaic arc. He connected one terminal of a galvanic pile with a plate of platinum, or of some other difficultly fusible metal, which he placed upon one of the poles of a powerful electro-magnet. If now the pointed end of a rod, of the same or of another metal, connected with the opposite end of the pile, was brought near the plate, and a luminous arc produced, a noise, not previously heard, and resembling that resulting from the discharge of a Leyden jar, was caused as often as the magnet was brought into play; at the same time, it was necessary to advance the point of the wire near to the plate, in order to keep up the luminous arc.

De la Rive explains this phenomenon by the *resistance* which matter, not sufficiently heated, opposes to the separation of its particles,—a resistance here produced by a peculiar change which results from the influence of a magnet upon the molecular constitution of the substance of the poles.

De la Rive justifies the assumption of such a change by adverting to the fact, that thick rods, not only of iron, but of any other metal, even thick columns of mercury, when placed upon the pole of a powerful magnet, begin to give sound, if a powerful, but interrupted electric current is passed through them.

Electro-thermal Decomposition.—Some time ago, Grove(2) recommended the employment of a platinum wire, rendered incandescent by an electric current, and inserted into the upper part of the eudiometer, for eudiometric purposes,—as peculiarly adapted to combine the gases rapidly or slowly, according as currents whose strength is varied by the introduction of resistances, are

(1) Arch. Ph. Nat. IV, 355. (2) Phil. Mag. 1841.

Electro-thermal decomposition.

applied; for by merely conducting the operation properly, a practised hand is able to combine the gases by explosion, or gradually, by a mere alteration in the intervals of contact.

A series of such experiments lately made by Grove with this eudiometer, conducted him to the important discovery that water is resolved into its gaseous constituents by red-hot platinum, whether heated by electricity or by other means(1).

Native osmium-iridium and palladium operated in a manner similar to that of platinum. Silica and other oxides experimented upon by Grove only yielded doubtful results. Grove is of opinion that the non-polar decomposition of water, first observed by Wollaston, which is produced during the discharge of an electric battery by platinum-points in water, depends upon the same cause, viz. that it is not the effect of electricity but of temperature.

As early as 1802, Sir Humphry Davy observed that whenever the electrodes of a powerful pile were brought into contact under water, concentrated sulphuric acid, nitric acid, alcohol, ether, ethereal or fatty oils, the moment of contact was marked by a development of vivid light and of gas. Poggendorff found on repeating these experiments(2) that the phenomenon disappeared on a closer union of the wires being effected, and did not occur if they were at any sensible distance from one another, but that there was an intervening point where the development of light and gas was at its maximum, without the slightest interruption of the continuity of the current(3). Poggendorff concluded that the phenomenon was an effect of the heat produced by the current, and consequently identical with that observed by Grove. The above-mentioned liquids were easily decomposed, on passing through them a platinum wire of sufficient tenuity to be rendered incandescent under the influence of the current.

New Theory of Electricity.—Hare, of Philadelphia, attempts to do away with the electrical theories of Franklin, of Dufay, and of Ampère by objections which he considers of great importance, and endeavours to supersede them by another, according to which electrical phenomena are deducible from a statical or undulatory polarization dependent upon the antagonist polarity of the waves(4).

(1) Phil. Trans. 1847, 1; Phil. Mag. [3] XXXI, 20, 91; Pogg. Ann. LXXI, 194, 221.

(2) Pogg. Ann. LXXI, 226; Arch. Phys. Nat. V, 352 (in abstr.).

(3) Pogg. Ann. LXXI, 229.

(4) Phil. Mag. [3] XXXII, 461; Sill. Am. J. [2] V, 230, 343; VI, 45.

Electro-dynamics. Electro-dynamometer.—The law of the reciprocal action of electric currents, the fundamental law of electro-dynamics, given by Ampère, has not hitherto been based in all points upon accurate, and therefore indubitable, experimental proofs. This chasm in experimental electro-dynamics has been filled by W. Weber, who has proved the correctness of Ampère's law, in its entire extent, by accurate measurements(1). For this purpose he employed a peculiar instrument of his own, termed electro-dynamometer, and constructed in the following manner:—The two galvanic conductors, whose reciprocal action is to be observed, consist of two thin copper wires wound with silk, which are coiled up like multipliers on the exterior of two cylindrical frames. One of these rings encloses a space of sufficient size to receive the other without interfering with their free mobility. Electro-dynamics. Electro-dynamometer.

If a galvanic current be conducted through the wires of both rings, one exerts a rotatory influence upon the other, which is greatest when their centres coincide, and when the two planes parallel with the coils of the rings form a right angle with one another. The common diameter of the two rings is the axis of rotation.

That ring which is to revolve, is suspended by two long and thin connecting-wires, which pass perpendicularly to the ceiling, where they are attached to two insulated brass hooks. Two conducting-wires, in connection with the poles of an electrometer, are affixed to the same hooks. Thus the electric current reaches the ring, which moves without the slightest friction, or any other impediment to its rotation, beyond the moment of torsion, due to its bifilor suspension, which is proportional to the sine of the angle of rotation. The same or another electric current may be conducted through the immoveable ring. The deflections of the moveable ring, which are thus produced, are measured from a distance in the same manner as those occurring in the bifilor magnetometer. For this purpose a mirror is attached to the moveable coil. To prevent the mere influence of terrestrial magnetism from causing a rotation, the cylinder-axis must be made while at rest to coincide with the magnetic meridian.

We are obliged to refer the reader to the treatise for a more accurate description of the electro-dynamometer.

By conducting the same current through both rings of this apparatus, and also round a galvanometer-needle, and by calculating

(1) Paper read at the foundation of the Royal Saxon Society of Science, published by the Prince Jablonowski's Society, 1846, 209; Pogg. Ann. LXXIII, 193 (in abstr.).

Electro-dynamics. Electro-dynamometer.

the deflecting forces from the observed deflections, W. Weber succeeded in exhibiting experimentally the following laws, which hitherto had scarcely been more than hypothetical.

The electro-dynamic force of the reciprocal action of two conducting-wires, through which currents of the same intensity are conducted, is proportional to the square of this intensity.

The same laws hold good for electro-dynamic influences at a distance, as for those produced by magnetism.

The electro-dynamometer consequently possesses the property, that, when an electric current passes through both coils, the resulting deflecting force is proportional to the square of the intensity of the current, whereas, in the galvanometer the deflecting force is merely in simple proportion to the force of the current. W. Weber has made an ingenious application of this difference in the two instruments, in order to measure the force and duration of such electric currents, as, like the discharge of a Leyden battery, only last a very short time.

If a current of very short duration be passed round a magnet-needle, the action is proportional to the entire quantity of the electricity set in motion, or to the force of the current, multiplied by the duration. For the velocity of motion acquired by the needle is dependent both upon the accelerating force, and upon the time of the action. The former is in the ratio of the current-force, *i. e.* of the quantity of electricity, which simultaneously passes through each transverse section. Therefore, if the current-force increases, and the duration is proportionally diminished, *i. e.* if the quantity of electricity remains the same, we must always obtain the same deflection. We are consequently enabled directly to deduce only the quantity of electricity in this instance from the deflection observed. In order to determine the intensity, it is necessary to be acquainted with the duration of the current.

If the same current passes through both coils of the dynamometer, the corresponding deflecting force is in the ratio compounded of those of the duration and of the square of the intensity; therefore, for equal amounts of electricity, it is greater, the shorter the duration of the current. The simultaneous observation, then, of the deflection observed in the two instruments, leads to two equations independent of each other, the one containing the product of the duration into the intensity, the other the product of the duration into the square of the intensity, from which accordingly both values may be deduced.

Weber has attempted thus to measure the time of discharge of an electric battery, the discharge being effected by means of a moistened hempen cord of 7^{mm} in thickness. His experiments,

which, however, he only considers as preliminary, led to the conclusion, that the duration of the discharge was nearly proportional to the length of the moist cord, and amounted to 0·0816 seconds for 2 metres (l. c. pag. 226). This result is in no way opposed to the velocity of electricity ascertained by Wheatstone for the discharge through copper wire; if we consider that copper conducts many million times better than water. Electro-dynamics. Electro-dynamometer.

This combination of the dynamometer with the galvanometer is also of importance in reference to the physiological investigation of the excitement of nerves by galvanic currents. For it appears that continuous currents rapidly lose their effect, especially in the nerves of sensation, and that consequently in such experiments, repeated momentary currents should be employed. The impressions produced upon the senses depend less upon the duration than upon the intensity of the current, and it is necessary to be acquainted with both.

The electric dynamometer has this decided advantage over the galvanometer, that it may be employed for the determination of the intensity of a series of contrary currents, f. i. of induction-currents, with the same accuracy as for the determination of a current with the same permanent direction. For, if a current passes at the same time through the fixed and through the moveable coil, a reversion of its direction takes place at the same time in both. The deflections of the bifilor coil are therefore entirely independent of the direction of the traversing currents. By this means W. Weber has succeeded in observing induction-currents, which were produced in a coil of wire, by the vibratory motion of a magnetic bar of steel, struck so as to give rise to a sound.

General Law of Induction.—The electro-dynamic phenomena can neither be deduced from the law of Ampère, nor from the fundamental laws of electrostatics; the doctrine of electricity therefore presents three chief classes of phenomena, the intimate connection of which had not hitherto been demonstrated. This demonstration has now been given by Weber.

According to the view now universally adopted there are, in each elementary portion of a current, equal quantities of positive and of negative electricity, which move in contrary directions, and thus give rise to that disturbance and restoration of the electrical equilibrium which we term the *electric current*. It follows that in two elements of a current, subjected to special examination, four reciprocal influences of the electric masses have to be taken into consideration, viz. two repelling influences,—between the two positive, and between the two negative masses in the elements of the current,

General law of induction.

—and two attracting influences,—between the positive mass in the first and the negative mass in the second, and between the negative mass in the first and the positive one in the second element.

The resultant of these actions should, according to the well known laws of electro-statics, be zero, because the similar, mutually repelling masses are equal to the dissimilar, attracting masses, and act upon one another at the same distance. Weber has however shown, that if this resultant is to be correctly determined not only for the case of relative rest, but also generally for every motion of both electrical masses towards each other, an additional magnitude, dependent upon their mutual motion, must be added to the value which the electro-static laws assign to the force created by two electrical masses upon one another. In ascertaining this magnitude he availed himself of the following laws:—

1st. Electrical masses moving in contrary directions act less powerfully upon one another than those moving in the same direction.

2nd. Two electrical masses influence one another less (repelling or attracting according as they are similar or dissimilar), in proportion to the increase of the square of their relative velocity.

The former law results directly from the fact, that two elements of a current, which are in the same straight line coincident with their direction, repel or attract one another, according as the motion takes place in the same or opposite direction. The relative velocity, or the difference of the absolute velocities, of two masses is positive or negative, according as a mutual approximation or separation results. This difference of sign however exerts no influence upon the amount of the mutual influence. The amount of force, therefore, depends upon a power expressed by an even number, or, in the first instance, upon the square of the relative velocity.

Proceeding upon these laws, Weber arrived at a mathematical expression, from which the fundamental laws of electro-statics and electro-dynamics are both deducible with the same accuracy, while there results from it, by necessity, a general law for the phenomena of induction.

Torsion-Balance for the Measurement of Induction-Currents.—A. Lallemand(1) of Nismes describes a species of torsion-balance which he has constructed for the purpose, not only of observing the effects of induced currents upon one another, but also of measuring the force of their mutual attractions and repulsions. Helices of thin wire coiled spirally in one plane are attached to the moveable beam of the torsion-balance, and other fixed wire-coils are suitably arranged opposite to them. The ends of the moveable coils

(1) Ann. Ch. Phys. [3] XXII, 19.

are immersed, as in Ampère's apparatus, in mercury cups, which are placed perpendicularly under the torsion-wire. The friction is therefore not avoided in this instrument, so that it is not adapted to very delicate measurements. Lallemand has not obtained any new result by the aid of this apparatus. **Torsion-balance for the measurement of induced currents.**

On Induction-Currents. Elie Wartmann, of Geneva, has, in the course of several years, published six treatises under the title "*Sur divers phénomènes d'induction*"(1). In the first he communicates his experience on the character of the dependence of the induced currents upon the nature of the inducing currents. The experiments, however, date from the year 1842, and have been made with very imperfect instruments, so that they present no novelties.

The second treatise, dated March, 1845, "*Sur la non-interférence des courants électriques,*" is intended to refute an assertion of Marianini, made in 1839, that several electric currents are enabled to pass through the same conductor without materially interfering with one another. Careful attention to Ohm's laws, sufficiently developed for this purpose in 1845, might have served to assist in a more satisfactory solution of the question.

The third, fifth, and sixth treatises are, like the former, characterized by negative results.

If a flint glass prism be introduced between the poles of an electro-magnet, and a pencil of polarized rays be thrown upon it, the development of magnetism exerts no influence upon the position of the dark lines in the spectrum.

Neither statical nor dynamical induction exert any influence upon electrolysis.

Magnets are incapable of producing chemical effects. Induced currents exert no reaction upon the force (the total effect) of continuous electric currents.

The electric current is not propagated by radiation.

Electric and magnetic induction have, according to E. Wartmann's experiments, no perceptible influence upon the elasticity of bodies giving sounds.

In the fourth treatise, the author describes a *rheotrope* (commutator), which is made on the principle of Jacobi's commutator(2), but simpler. It is equally applicable to the conversion of continuous into intermittent currents, without changing their direction, as

(1) Ann. Ch. Phys. [3] XIX, 257, 281, 385; XXII, 5, 10; XXIV, 213, 360; also Archives d'Electricité, IV, 34; V, 440; Arch. Phys. Nat. IV, 49; V, 143; VII, 287; VIII, 177.

(2) Mémoire sur l'application de l'électromagnétisme au mouvement des machines, Potsdam, 1835; also Pogg. Ann. XXXVI, 366.

On induction-currents. with variations in their direction; it also serves to obtain either of the two induction-currents separately, or to conduct both in the same direction. We are unable to describe this useful apparatus more minutely without the assistance of a drawing, we therefore refer the reader to the treatise itself(1).

Magneto-electrical Machine.—Many observers who have availed themselves of the magnetic-electro apparatus for the production of electric currents, have observed that the excitation of the current does not keep pace, as might have been supposed, with the velocity of rotation. In numerous cases, indeed, a maximum of the current-force has been observed to attend a certain velocity of rotation. This deportment has been explained by assuming that the production and disappearance of the magnetism in the iron cores requires a certain time. This explanation has, however, been proved by Lenz(2) to be sufficient for those cases only, in which the induction-currents set up are of a very low intensity, when, for instance, they have to pass through a great length of wire in addition to the coils in which they are developed.—On the other hand, in the case of currents, which have only to surmount comparatively slight external resistances, their force increases, for equal velocity of rotation the more slowly, and, as this velocity increases, attains a maximum the sooner, the smaller the external resistance.

Lenz accounts for this phenomenon by the reaction of the induced currents upon the iron cores, by which magnetism is reproduced in the latter; the maximum of this magnetism coincides with the maximum of the current-force; not, however, for that very reason, coinciding with the maximum of the primary magnetism of the iron cores induced by the magnet, it consequently causes a deviation of those points of the rotation in which the induced current-force is at zero, or a maximum. The amount of deviation increases with the force of the current, and consequently with the velocity of rotation. It is therefore clear, why, in the commutators of the machine, which are empirically adjusted for the development of the greatest current-force (always in the same direction), the change does not take place at the moment when the iron cores are opposite to the poles of the magnet; if the matter be only superficially examined, this is the instant at which the iron cores might be supposed to have attained the greatest possible degree of magnetism, and at which the induction in the copper wires would be at zero.

(1) Arch. Ph. Nat. V, 143; Ann. Ch. Phys. [3] XXII, 5; Phil. Mag. [2] XXXI, 241.
(2) Petersb. Acad. Bull. VII, 257.

INORGANIC CHEMISTRY.

Generalities. Catalysis.—Playfair(1) has communicated a paper upon the chemical processes in which the co-operation of catalytic forces is assumed. He is of opinion, that in many cases, the so-called catalytic power is identical with ordinary chemical action, and that the attraction of the substance, acting catalytically, is exerted in the same direction as that of the body undergoing decomposition, or entering into combination; under circumstances, however, in which the former alone cannot be satisfied. A body is stated to be endowed with catalytic power, when it acts, by adding its own attraction to that of another body, or by exerting an influence sufficient under certain conditions, to produce decomposition, but insufficient to overcome various powers, such as elasticity and cohesion, whose action may change the anticipated result. Our space will not allow us to follow in detail the individual cases adduced by Playfair in order to elucidate his ideas. The following quotation of his view respecting a process which he considers as catalytic, may serve as an illustration. Nitric acid, for instance, will not oxidize a body A, whose attraction for oxygen is insufficient to decompose this acid; on adding, however, a substance B, which likewise possesses an attraction for oxygen, the sum of their united attractions is capable of decomposing nitric acid. The oxygen which is removed from it, passes, however, entirely to the body A, endowed with the stronger attraction; B, remaining unchanged, appears to act by catalysis, *i. e.* by contact only, though it is by its ordinary chemical attraction that the reaction is induced. Generalities. Catalysis.

Influence of high Temperatures upon compound Gases.—Grove(2) has examined the influence of a platinum wire, maintained in a state

(1) Phil. Mag. [3] XXXI, 192.
(2) Ibid. 20, 91, 96; Ann. Ch. Phys. [3] XXI, 129; Ann. Ch. Pharm. LXIII, 1; Arch. Ph. Nat. V, 18, 112.

Influence of high temperatures upon compound gases.

of ignition by voltaic electricity, upon surrounding gases. Binoxide of nitrogen, confined over water, is decomposed into nitrogen and nitric acid (when confined over mercury, nitrous acid is formed), protoxide of nitrogen splits into oxygen and nitrogen; ammonia into nitrogen and hydrogen; olefiant gas, partially only, into carbon and hydrogen. Carbonic acid is not altered.

Decomposition of Water by Heat.—Water and steam are decomposed into oxygen and hydrogen. This decomposition succeeds, likewise, with platinum ignited by means other than electricity(1). A platinum wire, fused at the end to a ball of the size of a small pea, and heated in the oxyhydrogen-blowpipe-jet to near its fusing temperature, when suddenly plunged into water, evolves a mixture of oxygen and hydrogen. Steam is likewise decomposed when conducted through a white-hot tube of platinum, or by the influence of electric sparks passing from one pole to another.

Wilson(2) has discussed the question, how far Grove's experiments prove the decomposition of water in the same circumstances under which it is produced from its constituents. He observes, that proto-sesquioxide of iron, as produced by combustion of iron in oxygen, when heated to whiteness, evolves bubbles of gas from water; he at first believed that, in this case, a decomposition of water by heat might be assumed, but by accurate experiment, he found the evolved gas to consist of hydrogen, while an admixture of metallic iron was found in the oxide.

Comportment of Anhydrous Acids towards Vegetal Colours.—The deportment of anhydrous acids towards vegetal colours, f. i., litmus, has been investigated by Wilson(3). The fact that anhydrous hydrogen-acids, f. i. hydrochloric acid, redden litmus paper, while oxygen-acids produce no action except when in the state of hydrates, has been adduced as an argument in support of the view, that the so-called hydrates of oxygen-acids should rather be regarded as hydrogen-acids. A series of experiments has been conducted by Wilson, with the purpose of testing the correctness of this view. Perfectly dry gaseous sulphurous acid does not redden litmus-paper, even when allowed to remain in contact for a considerable time; the same deportment, however, is likewise observed with dry hydrosulphuric acid. Wilson remarks that, in such experiments, it is not only the absence of water that influences the results, but other

(1) Ann. Ch. Phys. [3] XIX, 253; Pogg. Ann. LXX, 447.
(2) Chem. Soc. Mem. III, 332; Phil. Mag. [3] XXXI, 177.
(3) Chem. Soc. Qu. J. I, 332.

Comportment of anhydrous acids towards vegetal colours.

circumstances also; f. i., that aqueous sulphurous acid acts in the liquid state; anhydrous, however, usually in the form of gas. In order to obtain results more comparative respecting the action of anhydrous liquid sulphurous acid, he placed litmus-paper in contact with the liquid, taking the greatest precaution to exclude every trace of moisture. At first, the blue colour of the paper was not altered; after 4 to 5 hours it was changed to a dark purple; in twenty hours it had been reddened. Wilson believes that the sulphurous acid decomposes the organic matter of the paper, and that by assuming the elements of water, it thus acquires the property of reddening litmus, while anhydrous liquid sulphurous acid has no action upon it. He believes that facts such as these are not likely to lead to conclusive views respecting the chemical constitution of acids.

Views regarding the Salts.—Gerhardt(1) has published investigations upon the salts. He adverts to the influence exerted by the order in which two salts are mixed upon the product obtained, which may differ according as the one is added in large excess to the other, or *vice versâ*. The influence of temperature and the presence of water is likewise considered. He defends the view that acids and bases must not be separated from the class of compounds called salts exclusively. Salts are molecular systems containing either hydrogen, or a metal which may be exchanged for another metal or hydrogen(2). The notation: neutral, basic, and acid salts, is arbitrary; more appropriate would be the term *équisels* for compounds corresponding to combinations of equal volumes of hydrogen and a non-metallic body (hydrochloric acid for instance), or to equal volumes of water, and of a so-called anhydrous acid (hydrated sulphuric acid for instance); *soussels* and *sursels* would represent compounds containing the elements of an *équisel* respectively, plus or minus a quantity of metallic oxide.

Oxygen.—Keller(3) has published some experiments, showing that an evolution of oxygen takes place when chloride of lime is boiled with water.

Some observations have been published by Kolbe(4) upon the oxidizing influence of oxygen when liberated in the circuit of the galvanic current. By the decomposition of a concentrated solution of

(1) J. Pharm. [3] XII, 57; Ann. Ch. Pharm. LXIV, 284.
(2) Respecting this view, compare Liebig's Memoir upon the Constitution of Organic Acids, Ann. Chim. Pharm. (1838) XXVI, 181.
(3) Reert. Pharm. [2] XLVII, 69.
(4(Phil. Mag. [3] XXX, 334; Chem. Soc. Mem. III, 285; J. Pr. Chem. XLI, 137; in abstract, Ann. Ch. Pharm. LXIV, 236.

Oxygen. sesquichloro-carbo-hyposulphate of potassa, crystals of perchlorate are separated ($KO, C_2 Cl_3 S_2 O_5, + 12 O = KO, Cl O_7 + 2 SO_3 + 2 CO_2 + 2 Cl$). In a solution of chloride of potassium, even in presence of sulphuric acid, chlorate, and finally perchlorate of potassa are formed. Cyanide of potassium is converted into cyanate of potassa. By employing a concentrated solution of chloride of ammonium, the positive pole, consisting of a plate of platinum, is covered with small drops of chloride of nitrogen.

Ozone.—Some observations and experiments on ozone have been published by Williamson(1). He critically examines the view adopted by Schönbein, and is inclined to consider ozone as a peroxide of hydrogen. He explains its formation by the action of phosphorus upon steam and oxygen, according to Liebig's view, respecting the induction of chemical combination, by the transference of chemical action. The combination of phosphorus with oxygen occasions a simultaneous formation of peroxide of hydrogen by the union of water and oxygen.

Some experiments on the action of ozone, chlorine, and bromine upon salts of manganese, and basic lead-salts, have been communicated by Schönbein (2). Ozone, produced either by means of phosphorus, by galvanic decomposition of water, or by frictional electricity, decomposes solutions of the salts of protoxide of manganese with separation of hydrated binoxide. Paper moistened with such a solution becomes brown. Under the influence of solar radiation, chlorine- and bromine-water act in the same manner, though more slowly. Chlorine- and bromine-water, or atmospheric air impregnated with ozone, produce from basic acetate of lead brown binoxide of lead. Solutions of the salts of protoxide of manganese may thus be employed as sympathetic inks; writing of this kind, when exposed to the vapour of ozone, immediately becomes brown(3); the colour disappearing after some time, will re-appear when again exposed to ozone(4). Solutions of protoxide of manganese in contact with air and phosphorus (when at a temperature of 15^0 to 20^0 ozone is produced) become of a columbine red. A similar change takes place on agitating the solution of protoxide of manganese, previously mixed with phosphoric, or the so-called phosphatic acid, in air, containing ozone; this is, according to Schön-

(1) Ann. Ch. Pharm. LXI, 13.
(2) Pogg. Ann. LXXII, 450.
(3) Ibid. 457; Phil. Mag. [3] XXXI, 176; J. Pr. Chem. XLII, 383.
(4) Ibid. LXXV, 366.

Ozone.

bein(1), occasioned by the formation of permanganic acid. Under similar circumstances, binoxide of lead, chlorine- and bromine-water, employed instead of ozone, give rise to a red colour.

Schönbein has published(2), moreover, some recent experiments upon the presence of ozone in the atmosphere. A mixture of starch-paste and iodide of potassium became gradually blue in the open air; paper moistened with sulphate of protoxide of manganese slightly changed to brown, in the same manner as in air impregnated with ozone; this does not, however, take place in confined air. He considers it very probable that the proportion of ozone in the atmosphere stands in intimate relation to the prevalence of catarrhal affections.

While no ozone is produced by phosphorus in moist oxygen, at the ordinary temperature and density of the air, it is formed, according to Schönbein(3), in oxygen rarified, or heated above 24°; generally under those conditions under which phosphorus becomes luminous in oxygen.

In connection with his researches on ozone, Schönbein(4) has published a memoir on the various chemical conditions of oxygen. He endeavours to establish the view, that oxygen may exist in two different states, in the ordinary form, and in the state in which it is more inclined to enter into chemical combination; the latter form he distinguishes by the term oxylized oxygen. He mentions those compounds in which he supposes the presence of oxylized oxygen, and communicates some views of his own respecting the composition of several oxygenated bodies; he expresses some doubts regarding the supposition, that ozone is oxygen in a peculiarly modified state, and hints at some conclusions which are likely to emanate from this view when more completely developed.

Some experiments have been described by Osann(5), according to which no ozone was produced by the electrolysis of pure water; whilst the diffusion of frictional electricity into an atmosphere of hydrogen gave rise to the odour of ozone. He found that ozone-odour was invariably produced, whether the frictional electricity was discharged either from platinum, copper, brass, or iron. He considers that these experiments are equally unfavourable to the view, that ozone is an oxide of either hydrogen, or nitrogen, and asks, whether the electrical ozone-odour in reality belongs to the same substance which is obtained in chemical processes.—In a more

(1) Pogg. Ann. LXXII, 459.
(2) Ibid. 462.
(3) Ibid. LXXV, 367.
(4) Pogg. Ann. LXXI, 517.
(5) Ibid. LXXI, 458.

Ozone. recent communication(1) he acknowledges the identity of phosphorus-ozone, and that which is generated by electricity; he farther describes experiments made to ascertain what aqueous solutions yield ozone on electrolysis, and adds some observations on ozonized air generally, (for the preparation of ozonized oxygen, he recommends the electrolysis of a concentrated solution of sulphate of zinc containing undissolved crystals.)

Water.—For "decomposition of water by heat," see Report, p. 248.

Tilghman(2) has communicated some observations (partly known previously) upon the decomposing power of steam at high temperatures. If the vapour of water be conducted over chloride of calcium, chloride of barium, or chloride of strontium, at a strong red heat, hydrochloric acid is formed, while pure lime, strontia or baryta will remain behind; at a dull red heat it expels the acid from sulphate of magnesia, at a red heat from sulphate of lime, at a moderate white heat from sulphate of baryta, and at a strong white heat, though slowly, from basic phosphate of lime. Magnesia, lime, and particularly alumina, greatly facilitate the decomposition of sulphates of potassa and soda, and of chlorides of sodium and potassium. Alum is decomposed completely, and at its fusing point, even felspar so far, that the powdered mass yields a solution of a strongly alkaline reaction, from which crystals of alum are deposited on addition of sulphuric acid.—Solly(3) has communicated farther details respecting Tilghman's patent process for obtaining, by the action of steam on common salt mixed with lime or alumina, a product which, on treatment with water, yields a strongly alkaline ley.

Hydrates.—Some researches on the influence of water upon the acid or basic character of chemical compounds have been published by Fremy(4). He arrives at the following conclusions: 1stly, that in most cases, it is not the presence of water on which the acidity of acids depends, since many acids may be reduced to the anhydrous state, without losing the faculty of combining with bases, and of expelling weaker acids from their combinations; 2ndly, that several hydrates, for instance, protoxides of tin and copper, sesquioxide of chromium, which comport themselves as weak acids, owe this pro-

(1) Pogg. Ann. LXXV, 386.
(2) From Trans. Amer. Phil. Soc. X, 2, Chem. Gaz. 1848, 180.
(3) Pharm. J. Trans. VII, 416; Sill. Am. J. [2] VI, 260, (in detail).
(4) J. Pharm. [3] XI, 169; (in abstract), Ann. Ch. Pharm. LXIV, 223; J. Pr. Chem. XL, 355; Ann. Ch. Phys. [3] XXIII, 385; (in full), J. Pr. Chem. XLV, 193.

perty to the presence of water only: when deprived of it they are no longer soluble in alkalies; 3rdly, that the acid character of metastannic acid (anomalous binoxide of tin) is entirely due to the water it contains; that this, however, is not the case with stannic acid (normal binoxide of tin); 4thly, that the basic character also of metallic oxides appears to be influenced by the presence of water; for instance, hydrated suboxide of copper forming salts with the same acids which decompose anhydrous suboxide. We here quote from Fremy's memoir only his conclusions relating to the action of water, referring for the other details to the several articles on hydrated suboxide and protoxide of copper, sesquioxide of chromium, stannic and antimonic acids. Hydrate

Carbon.—Jacquelain(1) has performed some experiments upon the effects of high temperatures upon diamond and coke; diamond was softened and coked by the heat produced between the charcoal points of a Bunsen's battery, consisting of 100 elements; thus converted, it exhibited a spec. grav. = 2·678, having had before the experiment a spec. grav. = 3·336: although friable, it yet remained sufficiently hard to scratch glass. A diamond, when heated in an atmosphere of carbonic acid by an oxy-hydrogen, or an oxy-carbonic oxide blowpipe, gradually disappeared without being softened; a similar deportment was observed with hard coal, which, however, even after continuous ignition in chlorine, still exhibited the presence of impurities, which fused into globules yielding with soda a transparent bead.

Some experiments have been made by Schönbein(2) on the absorption of chlorine and vapours of bromine and iodine by vegetal charcoal, and on the action of the latter upon hydrated nitric and hyponitric acids.

Carbonic Acid.—R. E. and W. B. Rogers(3) have observed that at the temperature of 180° to 230°, diamond is completely converted into carbonic acid, by a mixture of bichromate of potassa and sulphuric acid.

The comportment of solid carbonic acid with bases has been described by Channing(4); when placed in contact with hydrates of potassa and soda, sufficient heat is evolved to inflame gun-cotton. With caustic baryta, strontia and lime, oxides of lead, zinc and copper, no increase of temperature is perceptible; with their hydrates,

(1) Compt. Rend. XXIV, 1050; Ann. Ch. Phys. XX, 459.
(2) Pogg Ann. LXXIII, 326.
(3) Instit, 1848, 379; Sill. Am. Journ. [2] VI, 110.
(4) Sill. Am. J. [2] V, 184; Chem. Gaz. 1848, 177.

Carbonic acid.

a slight evolution of heat takes place, which, however, in the case of the last three oxides is scarcely appreciable.

The absorption of carbonic acid by water at different temperatures has been investigated by W. B. and R. E. Rogers(1): 100 vol. of water absorb, according to these observers, the barometer being at 30 English inches, the following vol. of carbonic acid:

at 0°	4°·4	10°0	15°·6	21°·1	26°·7	32°·2	37°·8	65°·6
175·7	147·9	122·2	100·5	83·8	68·6	57·5	50·3	11·4 vol.

the latter volumes reduced to 15°·6. Water, even when boiling under the same atmospheric pressure, still absorbed a perceptible quantity of carbonic acid.

W. B. and R. E. Rogers(2) have farther observed that hydrated sulphuric acid at 16°, absorbs 94 vol. of carbonic acid, while the fuming acid dissolves not less than 125 per cent. With reference to their observations, Noad(3) has published some experiments, by which it appears that the quantity of carbonic acid absorbed in analysis by its passage through sulphuric acid may be neglected. In consequence of this statement, W. B. and R. E. Rogers(4) have again made some experiments, to prove that hydrated sulphuric acid, by continuous contact with carbonic acid, (by the passage of a rapid current, for instance,) is capable of absorbing 76 vol. per cent., which are not completely expelled even at temperatures above 100°; with regard to the absorptive power of fuming sulphuric acid, they adhere to their former statements.

Propositions have been made by Mohr(5) for the best method of preparing carbonic acid solutions. Du Mênil(6), Mohr(7), and Gräger(8) have exchanged their views respecting the utility or inutility of these pharmaceutical agents.

Lassaigne(9) has found that one part by weight of the following carbonates is dissolved at 10° by the annexed quantities of water, saturated with carbonic acid:

(1) Sill. Am. J. [2] VI, 96.
(2) From Ed. Monthly Journal, Feb. 1848, in Chem. Gaz. 1848, 113.
(3) Chem. Gaz. 1848, 671.
(4) Ibid. 477.
(5) Ann. Ch. Pharm. LXI, 81.
(6) Arch. Pharm. [2] LI, 23; LIV, 8.
(7) Ibid. [2] LIII, 44.
(8) Ibid. [2] LV, 159.
(9) J. Chim. Méd. [3] IV, 312; J. Pr. Chem. XLIV, 247.

Carbonate of lime by	1136	Carbonic acid.
„ baryta by	588	
„ strontia by	833	
„ protoxide of manganese by	2500	
„ protoxide of silver by	961	
„ protoxide of zinc by	1428	
„ hydrated carbonate of protoxide of copper by	3833	
„ carbonate of protoxide of lead by	7144	

At 0^0, one part of carbonate of lime dissolved in 1428 parts of carbonic acid water. With this variation of solubility, it is very improbable that (as Lassaigne imagines) a definite stoechiometrical relation exists between the quantity of carbonic acid contained in the neutral salts and the solvent employed.

According to J. Davy(1), water which has been saturated, under pressure, with carbonic acid, dissolves an appreciable quantity of phosphate of lime (see phosphate of lime). Gypsum does not dissolve in it more readily than in pure water, while alumina remains perfectly intact.

Boron. Borates.—A synopsis of the composition of the borates, according to the views of Laurent and Gerhardt(2), has been given by the former.

Biborate of Soda.—Bolley(3) has observed that free ammonia is evolved on mixing solutions of borax and chloride of ammonium, employed in the proportion of two equivalents of the former to one of the latter; the solution, when slowly evaporated, deposits crystals, requiring five or six parts of water for solution, and exhibiting the composition $NaO, 4BO_3 + 10HO$. The solution has no action upon either litmus or turmeric paper; on addition of dilute sulphuric or nitric acid, a white precipitate of boracic acid is produced. By an excess of chloride of ammonium, borax is completely converted into common salt and boracic acid. Bolley is of opinion, that the native boracic acid may be produced by the action of chloride of ammonium upon minerals containing this acid.

Phosphorus. Amorphous modification of Phosphorus.—Schrötter(4) has found that the red colouration which phosphorus assumes when exposed to light, does not arise from oxida-

(1) Edin. new Phil. Journ. XLV, 61. (2) Compt. Rend. XXIV, 94.
(3) Chem. Gaz. 1849, 60; Ann. Ch. Pharm. LXVIII, 122; J. Pr. Chem. XLVI, 410.
(4) Wien. Acad. Ber. I, 1848, 130; Ann. Ch. Ph. [3] XXIV, 406; Compt. Rend. XXVII, 427 (in abstract); Ann. Ch. Pharm. LXVIII, 247.

Phosphorus. Amorphous modification of phosphorus.

tion, but is due to the formation of a new, amorphous modification, which had been anticipated by Berzelius. The latter modification is obtained in considerable quantity whenever phosphorus, in an atmosphere in which it cannot oxidize, is persistently exposed (for about fifty hours) to a temperature approaching its boiling point, (240° to 250°). The fused phosphorus, colourless and transparent in the beginning of the experiment, becomes red and opaque; the amorphous modification may be separated from the ordinary one by bisulphide of carbon, in which the former is insoluble. Amorphous phosphorus, when dry, forms a lustreless, scarlet or carmine powder, the colour of which darkens on heating; its specific gravity at 10° is 1·964, exceeding that of ordinary phosphorus. (According to Schrötter, the specific gravity of ordinary phosphorus in the solid state at 10° is from 1·826 to 1·840, in the liquid state at 45°, 1·88). The amorphous modification becomes luminous in the dark only at a temperature close to its point of inflammation (260°); it is either insoluble or only slightly soluble in the solvents of ordinary phosphorus; it combines with chlorine without evolution of light. The combination with bromine is attended with light. Dilute potassa-solution acts very slowly on amorphous phosphorus even on ebullition; concentrated potassa dissolves it with evolution of pure uninflammable phosphoretted hydrogen. When heated, it is reconverted into the ordinary phosphorus, which distils over. Incidentally to this investigation, Schrötter has carefully examined the boiling points of phosphorus under several pressures. He obtained the following results:

120mm	165°	204mm	180°	339mm	209°	393mm	226°
173	170	266	200	359	218	514	230

Napoli(1) is of opinion that the yellow colouration and imperfect transparency of phosphorus does not necessarily arise from any impurity, but may be founded on a peculiar molecular condition. He appears to believe that it depends on the temperature of the water in which phosphorus is melted, whether this substance solidifies yellow and translucent, or colourless.

According to Schönbein(2), phosphorus-vapour, as such, is inodorous, and the odour which phosphorus possesses is a mixed one, arising simultaneously from ozone and phosphorous acid.

Phosphoric Acid.—Our knowledge of phosphoric acid has been considerably extended during the years 1847 and 1848. Several modifications of this acid, until then unknown, have been investigated.

(1) Compt. Rend. XXV, 369. (2) Pogg. Ann. LXXV, 377.

H. Rose(1) has given a synopsis of the isomeric states of phosphoric acid, and has investigated more fully the reactions of these modifications, particularly of their soda-compounds, in addition to various facts, to be farther noticed in the following pages. Phosphoric acid.

Common phosphoric Acid.—With respect to common phosphoric acid, Rose has called attention to the fact that many insoluble phosphates are soluble in an excess of the saline solution in which they are produced by precipitation with phosphate of soda; the solution thus obtained possesses generally the property of yielding, when heated, a considerable precipitate, which disappears again on cooling. Rose considers this deportment as particularly characteristic of common phosphoric acid. In employing an excess of pyrophosphate of soda, the precipitate first formed may likewise be dissolved, and a turbidity produced on application of heat. This turbidity, does not, however, disappear on cooling.

Phosphate of Soda.—According to Gerhardt(2), the phosphate of soda, $3\,NaO, PO_5$, still retains 1 equivalent (5·2 per cent) of water at 100°, so that when dried at this temperature, it is $3\,NaO, PO_5 + HO$; this water is not even perfectly expelled at 200°, but only by heating to redness(3); the ignited salt again takes up with avidity this 1 equivalent of water; when slightly moistened, it evolves a considerable amount of heat. He states that the corresponding baryta- and lime-compounds likewise retain water at 200°.

Phosphate of Lithia.—Rammelsberg(4) has found that common phosphoric acid enters into at least three combinations with lithia. $3\,LiO, PO_5$ is obtained by addition of phosphate of ammonia and free ammonia to an acid solution of acetate of lithia, or of phosphate of ammonia only to a neutral solution of the latter salt, or by heating carbonate of lithia with water and a slight excess of phosphoric acid; it forms a crystalline powder, containing 1 equivalent of water of crystallization, which is expelled before heating to redness. This salt is soluble in 833 times its weight of water at 12°, and does not fuse on being heated. A compound $3\,LiO, PO_5 + 2\,LiO, HO, PO_5 + 2\,HO$ is formed on precipitating chloride of lithium with phosphate of ammonia. It is a crystalline powder, soluble in 200 times its

(1) Berl. Acad. Ber. Nov. 1848, 409; Instit. 1849, 135; Arch. Ph. Nat. X, 310; complete in Pogg. Ann. LXXVI, 1; Phil. Mag. [3] XXXIV, 321.

(2) J. Pharm. [3] XII, 63.

(3) According to Graham's former experiments this, takes place only after repeatedly pulverizing and igniting it.

(4) Berl. Acad. Ber. Nov. 1848, 385; Instit. 1849, 103; more in detail. Pogg. Ann. LXXVI, 261.

Phosphate of lithia. weight of water, which loses 2 equivalents of water at 100°. $LiO, 2HO, PO_5$ may be produced by dissolving the first of the above-named salts in nitric acid, evaporating the excess of this acid, dissolving the residue, and crystallizing, or by heating carbonate of lithia with excess of phosphoric acid, and evaporating the liquid separated from the precipitate formed, or by evaporation of a solution of neutral acetate of lithia with phosphoric acid. It forms pretty large, easily soluble crystals, deliquescent in air, and parting with no water at 100°, but with 1 equivalent at 200°, when they are converted into pyrophosphate.

Phosphate of Baryta.—According to Ludwig(1) the precipitate obtained with common phosphate of soda and chloride of barium—in whatever order the solutions be mixed, and whichever be in excess—is $2BaO, HO, PO_5$; one part of this salt by weight is soluble in 4362 parts of water, containing 1·2 per cent. of chloride of sodium, and 0·8 of chloride of barium. If this precipitate be dissolved in hydrochloric acid, and reprecipitated by ammonia, a portion of the phosphoric acid remains in solution, and the precipitate produced contains chlorine, which cannot be removed by washing, but is present in variable quantities; the product of one preparation was found soluble in 17912 parts by weight of pure water, and in 3495 of water containing chloride of barium, chloride of ammonium and ammonia; when dried in air it was found to correspond to $15BaO, 6PO_5 + BaCl + 6HO$.

Phosphate of Magnesia and Ammonia.—Boussingault(2) recommended the addition of a salt of magnesia (for instance, chloride of magnesium) to putrefying urine, in order to collect both the phosphoric acid in the urine and the ammonia formed, and to obtain, in the deposited phosphate of magnesia and ammonia, an efficient manure. A similar proposal had previously been made by R. A. Smith(3).

Phosphate of Lime.—Raewsky(4) agrees with the view already previously proposed, that the so-called artificial bone-earth is not $8CaO, 3PO_5$ (which composition had been ascribed to it by Berzelius), but $3CaO, PO_5$. The latter formula, however, does not represent the composition of phosphate of lime contained in bones, since a larger quantity of phosphoric acid has been obtained in the analysis

(1) Arch. Pharm. [2] LVI, 265; Ann. Ch. Pharm. LXVIII, 254 (in abstract).
(2) Ann. Ch. Phys. [3] XX, 117.
(3) Chem. Soc. Mem. III, 302.
(4) Compt. Rend. XXVI, 205; Instit. 1848, 125.

of certain bones. The acid phosphate of lime CaO, 2 HO, PO_5, is decomposed by alcohol into free acid and a phosphate, which, however, is not neutral phosphate of lime, but contains 3 CaO, 2 PO_5, 4 HO. The precipitate formed in the decomposition of chloride of calcium, by phosphate of soda, is not always of the same composition; a solution of chloride of calcium being added to a solution of phosphate of soda produces 2 CaO, PO_5, 4 HO, while, on addition of a solution of phosphate of soda to that of chloride of calcium, a precipitate of 2 CaO, PO_5, 5HO is formed.—Baer(1) has examined the deportment of phosphate of lime with acetic acid, in which this compound is sometimes perfectly soluble. He found that by adding a solution of phosphate of soda to chloride of calcium solution (an excess of the former being avoided), a precipitate was formed, yielding, with acetic acid, a solution remaining clear even after the lapse of some time. The precipitate produced by an excess of phosphate of soda was likewise soluble in acetic acid, the solution, however, deposited crystals after some time. Baer prepared a quantity of these crystals by mixing a solution of phosphate of soda with acetic acid, and adding a solution of chloride of calcium. The crystalline precipitate, when washed, was easily soluble in nitric and hydrochloric acids, but difficultly so in acetic acid and water. When dried over sulphuric acid, it was found to have the composition 2CaO, HO, PO_5 + 4 HO.

Phosphate of lime.

Liebig(2), with reference to the opinion which he formerly expressed, that phosphate of lime was soluble in water containing chloride of sodium, ammoniacal salts, or carbonic acid, and was thus conveyed to the plants, has now more minutely stated that 1 litre of water, saturated with carbonic acid, dissolves 0·6626 grm. of bone-earth, of which 0·500 grm. is deposited on boiling.—Lassaigne(3) states that water containing its own volume of carbonic acid, dissolves, by contact during twelve hours at 10°, 0·000750 of artificially prepared basic phosphate of lime, 0·000166 phosphate of lime from fresh bones, and 0·000300 from bones that have been under ground about 20 years; farther(4), that 40 cubic centimetres of water, containing $\frac{1}{12}$ of their weight of chloride of sodium, dissolve 0·0127 grm. of basic phosphate of lime, and that the presence

(1) Pogg. Ann. LXXV, 152; Ann. Ch. Pharm. LXVIII, 255 (in abstract).
(2) Ann. Ch. Pharm. LXI, 128.
(3) J. Chim. Méd. [3] III, 11; IV, 536.
(4) Ibid. [3] IV, 599.

Phosphate of lime.

of chloride of ammonium in the water, still increases the solubility.—A. Crum(1) has ascertained the quantity of phosphate of lime ($3\,CaO, PO_5$) which is dissolved at 37°, by acids so diluted that they contain 1 equivalent of anhydrous acid, to 1000 equivalents of water. He finds 100 parts of nitric acid thus diluted, being left for two hours in contact with the phosphate, and frequently stirred, to dissolve from 0·747 to 0·768 of this salt; hydrochloric acid from 0·802 to 0·910; acetic acid from 1·10 to 1·12; tartaric acid from 1·26 to 1·33; malic acid from 0·899 to 940; lactic acid from 0·820 to 1·150; and sulphuric acid from 1·15 to 1·30; he endeavours to deduce stoechiometrical relations from these numbers.

Phosphate of Protoxide of Manganese.—According to Heintz(2), small prisms of $MnO, 2HO, PO_5 + 2HO$ separate from the syrupy aqueous solution of the mass obtained by heating phosphoric acid with binoxide of manganese till the latter is reduced, or from the solution in phosphoric acid of the precipitate formed by common phosphate of soda in a salt of the protoxide of manganese; they part with their water of crystallization at 120°, and are easily soluble in water, but difficultly so in alcohol; the latter withdraws phosphoric acid, and leaves a salt containing 2 atoms of base to 1 of acid. Heintz found the precipitate produced by common phosphate of soda in sulphate of manganese to be $3\,MnO, PO_5 + 7\,HO$; 4 HO escape at from 110° to 120°, the remainder being expelled only by a red heat. By the action of ammonia on this salt when freshly precipitated, the double salt $2\,MnO, NH_4O, PO_5 + 2\,HO$, discovered by Otto is produced; Heintz obtained the same compound by dropping a slightly ammoniacal solution of sulphate of manganese, mixed with chloride of ammonium into a solution of common phosphate of soda; the precipitate produced, at first gelatinous, soon changed into crystalline scales, possessing all the properties and the composition of Otto's double salt. On boiling phosphoric acid with an excess of the freshly precipitated salt $3\,MnO, PO_5$, the residue, remaining insoluble, assumed a crystalline texture, forming small white granular crystals of $2\,MnO, HO, PO_5 + 6\,HO$, losing 5 HO at from 110° to 120°; they are easily soluble in strong acids, difficultly so in acetic acid and water, and insoluble in alcohol. The same compound is formed, when to a solution of sulphate of manganese, acidified with acetic

(1) Ann. Ch. Pharm. LXIII, 394.

(2) Pogg. Ann. LXXIV, 449; LXXV, 174; Ann. Ch. Pharm. XLVIII, 257 (in abstract); Chem. Gaz. 1848, 488.

Phosphate of protoxide of manganese.

acid (hydrochloric or phosphoric acid) common phosphate of soda is gradually added, till the precipitate formed no longer disappears, manganese still remaining in solution; after filtration, the amorphous precipitate becomes crystalline, and the filtrate likewise deposits crystals of the above compound.

Herrmann(1) found the light brown-red crystals, which according to L. Gmelin are obtained by strongly heating binoxide of manganese with phosphoric acid, extracting with water, and evaporating the colombine-red solution, to be of varying composition. He found from 24·8 to 37·3 per cent of binoxide of manganese, and 49·4 to 49·9 per cent of phosphoric acid; for the peach-blossomed powder, which remained on extraction with water and was insoluble in acids, with the exception of hydrochloric acid, he ascertained the composition to be $Mn_2 O_3$, 3 PO_5, 2 HO.

Phosphate of Protoxide of Lead.—According to Heintz(2) the compound 3 (3 PbO, PO_5) + Pb Cl + HO is obtained, if a boiling solution of protochloride of lead be poured into a boiling solution of common phosphate of soda, the latter remaining in excess, the mixture agitated, boiled, and the precipitate washed with hot water, and dried at 130°. This compound is insoluble in water, difficultly soluble in concentrated nitric acid, but easily so in dilute; on ignition it loses water, but does not change in colour. If the phosphate of soda be added to the solution of protochloride of lead, the latter remaining in excess, another compound 2 (3 PbO, PO_5) + Pb Cl, not differing in appearance from the former, is produced, which turns yellow on being heated, before fusion, but becomes white again on cooling, until, when repeatedly ignited, it is converted by the elimination of a certain quantity of protochloride of lead, into the former compound, when it no longer turns yellow on being heated.—Heintz finds the precipitate produced by mixing aqueous solutions of nitrate of protoxide of lead and phosphate of soda, to be free from nitric acid, excepting when formed in the presence of pretty concentrated nitric acid; this precipitate has, however, no constant composition, inasmuch as (when dried at from 110° to 120°) it was found to contain from 74·7 to 81·9 per cent of protoxide of lead, from 17·7 to 22.6 of phosphoric acid, and from 0·4 to 2·7 of water; in all the analyses, the sum of the oxygen of the protoxide of lead and water,

(1) Pogg. Ann. LXXIV, 303; J. Pharm. [3] XIV, 399.

(2) Pogg. Ann. LXXIII, 122; Ann. Ch. Pharm. LXVIII, 287 (in abstract); J. Pr. Chem. XLII, 142; Berl. Acad. Ber. 1847, 227; Instit. 1848, 97; J. Pharm. [3] XIV 153.

Phosphate of protoxide of lead.

was nearly $\frac{4}{5}$ths of that in the phosphoric acid.—The compound 2 PbO, HO, PO_5 was produced by precipitating a boiling solution of nitrate of protoxide of lead with pure phosphoric acid; it is a beautiful, brilliant white crystalline precipitate, of the lustre of mother of pearl.—The compound 3 PbO, PO_5 was obtained in a state of purity, according to the methods described by Berzelius and Mitscherlich, namely, by incomplete precipitation of acetate of protoxide of lead with phosphate of soda, and dessication of the white amorphous precipitate at 130^0 (when its weight was scarcely diminished by ignition); or by digestion of 2 PbO, HO, PO_5 with ammonia.—The precipitate obtained by acid phosphate of soda from a hot solution of protochloride of lead, when dried at 110^0, was found to contain 19·6 phosphoric acid, 1·7 chlorine, 72·4 lead, and (by loss) 6·4 oxygen and water; on cooling after fusion it exhibited neither the phenomenon of crystallization nor that of incandescence.

According to Gerhardt(1), on the contrary, the addition of an alkaline phosphate to an excess of a boiling solution of protochloride of lead produces a crystalline precipitate 2 PbO, HO, PO_5 + Pb Cl, insoluble in water, and losing its constitutional water slowly at 100^0. He finds, that an alkaline phosphate, added to an excess of nitrate of protoxide of lead, produces a crystalline precipitate 3 PbO, PO_5 + PbO, NO_5 + 2 HO, insoluble in cold water, but crystallizing from nitric acid in six-sided plates, derived from an oblique rhombic prism; this salt is decomposed by boiling water into PbO, NO_5 and 3 PbO, PO_5, (which latter compound is likewise obtained by employing acetate of protoxide of lead, or by the addition of nitrate of protoxide of lead to an excess of an alkaline phosphate). On ignition to redness it yields 4 PbO, PO_5 without change of form(2).

Phosphate of Silver.—Schwarzenberg(3), by dissolving yellow phosphate of silver in phosphoric acid, and concentrating over sulphuric acid, obtained no crystals, even from the solution in the syrupy state; on the addition of ether, however, a white crystalline powder separated, which, when washed with absolute alcohol, gave the formula 2 AgO, HO, PO_5, and, as stated by Berzelius, was decomposed by water, into 3 AgO, PO_5 and free phosphoric acid; at 100^0 no water is expelled, but at 170^0 the conversion into pyrophosphate of silver takes place.

(1) Ann. Ch. Phys. [3] XXII, 505; Ann. Ch. Pharm. LXVIII, 286.
(2) J. Pharm. [3] XII. 58.
(3) Ann. Ch. Pharm. LXV, 161.

Pyrophosphates.—Schwarzenberg(1) has published investigations on the pyrophosphates. *Pyrophosphate of potassa,* 2 KO, PO_5 (fused) was obtained by mixing common phosphoric acid with an alcoholic solution of hydrate of potassa, so that the mixture had a slightly acid reaction, adding alcohol until the liquid became milky, concentrating and igniting the syrup which had deposited after standing 24 hours, and then separating the pyrophosphate of potassa from the insoluble metaphosphate, by treating the mass with water. The aqueous solution has an alkaline reaction, and may be boiled without being converted into common phosphate, which ensues, however, on addition of hydrate of potassa. The fused salt is a white mass, deliquescent on exposure to the air. The syrupy solution solidifies over sulphuric acid to a dazzling white radiated mass, 2 KO, PO_5 + 3 HO; 1 HO is expelled at 100^0, a second atom at 180^0 (without the salt being converted thereby into common phosphate), and the third atom is only perfectly driven off by ignition.—On dissolving this salt in acetic acid, and adding alcohol, the acid *pyrophosphate of potassa* separates as a syrup, solidifying gradually over sulphuric acid; it is white and deliquescent, its formula being KO, HO, PO_5; its aqueous solution has an acid reaction, and may be boiled without conversion into common phosphate.—If this salt be supersaturated with ammonia and evaporated over a mixture of caustic lime and chloride of ammonium, the white deliquescent *pyrophosphate of potassa and ammonia,* 2 KO, PO_5 + NH_4O, HO, PO_5 + HO is obtained, the solution of which, on boiling, yields the foregoing salt, with evolution of ammonia.—Schwarzenberg prepared the *acid pyrophosphate of soda,* NaO, HO, PO_5, by dissolving 2 NaO, PO_5 (fused or crystallized) in acetic acid, and adding alcohol, when it separated in the crystalline form; it may be obtained in larger crystals by pouring a layer of alcohol on the aqueous solution. — After saturation of this salt with carbonate of potassa and concentration to the consistency of a thin syrup, the mass, on cooling, is converted into a magma of fine, white, transparent needles of *pyrophosphate of potassa and soda,* KO, NaO, PO_5, + 12 HO.—Pyrophosphoric acid, supersaturated with ammonia, became turbid on the addition of alcohol, and, after the lapse of 24 hours, deposited *pyrophosphate of ammonia,* 2 NH_4O, PO_5, in arborescent groups of small needles. When heated with ammonia, this salt is converted into the common

(1) Inaugural dissertation: Researches on the Pyrophosphates, Göttingen, 1847; Ann. Ch. Pharm. LXV, 133; J. Pr. Chem. XLVI, 247; J. Pharm. [3] XIII, 311.

Pyrophosphates.

Pyrophosphates. phosphate; when boiled with water alone, it loses ammonia, becoming acid pyrophosphate, which is obtained crystalline, if the salt just spoken of be dissolved in acetic acid and alcohol added; when a thick syrup separates, which changes after a time into small crystalline plates of pearly lustre, consisting of NH_4O, HO, PO_5; these are easily soluble in water, the solution has an acid reaction, and is not altered by boiling.—If the acid soda-salt be dissolved in water, the solution supersaturated with ammonia, and evaporated over a mixture of caustic lime and chloride of ammonium, white prisms of *pyrophosphate of soda and ammonia*, $NaO, NH_4O, PO_5 + 5\,HO$ are formed, which are easily soluble in cold water; when boiled with it, they lose ammonia, being transformed into the acid pyrophosphate of soda.

Pyrophosphate of baryta, $2\,BaO, PO_5 + HO$ (when dried at 100°), is obtained by precipitating chloride of barium with pyrophosphate of soda, or baryta-water with pyrophosphoric acid, as a white amorphous powder, somewhat soluble in water, soluble in nitric and hydrochloric acids, insoluble in acetic acid and pyrophosphate of soda(1).—*Pyrophosphate of strontia* is formed by precipitating nitrate of strontia with pyrophosphate of soda in the cold. It is a white amorphous powder, which is converted into small crystals on being warmed in the mother-liquor; its properties are the same as those of the baryta-salt; when dried in the water-bath, it has the composition $2\,SrO, PO_5 + HO$; its water begins to escape when it is heated above 100°.—*Pyrophosphate of lime* precipitates on addition of pyrophosphate of soda to chloride of calcium as a white amorphous powder, which, when dissolved in a solution of sulphurous acid, forms crystalline crusts, when the sulphurous acid is driven off by heat; the solubility of this salt in various liquids is the same as that of the foregoing ones, its composition in the amorphous, as well as the crystalline state, when dried at 100°, being $2\,(2\,CaO, PO_5) + 3\,HO$(2).—*Pyrophosphate*

(1) According to Gerhardt, the composition of the pyrophosphate of baryta (dried at 100° ?) is $2\,BaO, PO_5 + 2\,HO$. (J. Pharm. [3] XII, 64).

(2) The precipitate produced on addition of chloride of calcium to an aqueous solution of pyrophosphate of soda, disappears, according to Baer, on addition of acetic acid, but with much greater difficulty than that obtained with common phosphate of soda; after some time (or immediately on addition of a solution of chloride of calcium) the pyrophosphate of lime $2\,CaO, PO_5 + 4\,HO$ separates in crystals; the same compound is formed as an amorphous precipitate by pyrophosphate of soda and an excess of chloride of calcium. By gradually dropping a solution of the latter salt into a boiling solution of pyrophosphate of soda, a crystalline precipitate, $CaO, NaO, PO_5 + 4\,HO$, is obtained. If, instead of chloride of calcium, solutions of chloride of barium,

of magnesia is precipitated from sulphate of magnesia by pyrophosphate of soda, even without the presence of ammoniacal salts, as an amorphous white powder, which may be obtained crystalline in the same manner as the foregoing salt; it is somewhat soluble in water, perfectly so in nitric and hydrochloric acids, and likewise in pyrophosphate of soda; the composition of the salt (dried at 100^0) is 2 MgO, PO_5 + 3 HO. Magnesia dissolves in a solution of acid pyrophosphate of soda, but, on heating, the pyrophosphate of magnesia separates.—*Pyrophosphate of alumina.* The aqueous solution of sublimed sesquichloride of aluminum, when precipitated with pyrophosphate of soda, yields an amorphous white mass, similar to hydrate of alumina; when dried at 110^0, it has the composition 2 Al_2O_3, 3 PO_5 + 10 HO. Pyrophosphates.

Pyrophosphate of soda produces in a cold solution of chrome-alum a dirty-red precipitate, in a boiling solution a light green precipitate of *pyrophosphate of sesquioxide of chromium,* which darkens on drying at 100^0, and has the composition 2 Cr_2 O_3, 3 PO_5 + 7 HO, when dessicated at 130^0.—Sulphate of protoxide of manganese yields with pyrophosphate of soda an amorphous white powder, *pyrophosphate of protoxide of manganese,* having the composition 2 MnO, PO_5 + 3 HO, when dried at 100^0; and 2 MnO, PO_5 + HO, when dried at 120^0.—*Pyrophosphate of protoxide of zinc* is obtained by the precipitation of sulphate of protoxide of zinc with pyrophosphate of soda as an amorphous white mass, shrinking on drying; it may be obtained crystalline by the same method as the lime-salt; the crystalline salt dried at 100^0 is 2 (2 ZnO, PO_5) + 3 HO. This salt is soluble in acids and alkalies; from the ammoniacal solution alcohol precipitates a syrupy mass.—*Pyrophosphate of protoxide of cadmium,* obtained by the precipitation of sulphate of protoxide of cadmium with pyrophosphate of soda, is a white heavy powder, separating from its solution in sulphurous acid in the form of small scales of nacreous lustre; when dried at 100^0 its composition is 2 CdO, PO_5 + 2 HO.—A salt of protoxide of iron, when mixed with pyrophosphate of soda, yields an amorphous white precipitate, becoming immediately greenish, and afterwards brown on exposure to air.—*Pyrophosphate of sesquioxide of iron* was obtained by precipitating a solution of sublimed sesquichloride of iron with pyrophosphate of

nitrate of strontia, sulphate of magnesia, or nitrate of silver were employed in the same manner, amorphous precipitates, containing soda, were produced, which could not be washed with pure or ammoniacal water, and could not be reduced to any simple stoechiometrical expression, so that they must be considered as mixtures. (Pogg. Ann. LXXV, 152; Ann. Ch. Pharm. LXVIII, 255, in abstr.)

Pyro-phos-phates. soda, as a slightly yellowish-white powder, having the composition $2 Fe_2 O_3, 3 PO_5 + 9 HO$, when dried at 110°.—*Pyrophosphate of protoxide of lead*, precipitated from acetate of protoxide of lead by pyrophosphate of soda, is an amorphous white powder of the composition $2 PbO, PO_5 + HO$ when dried at 100°(1).—*Pyrophosphate of protoxide of copper* is produced, by precipitating a solution of protoxide of copper with pyrophosphate of soda, as an amorphous greenish-white powder, becoming dark-blue at 100°; it may be obtained crystalline from its solution in aqueous sulphurous acid; whether amorphous or crystalline, when dried at 100°, it has the formula $2 CuO, PO_5 + 2 HO$. If the salt be dissolved in ammonia, and the solution covered without admixture by a layer of alcohol, ultramarine-coloured nodular crystals are formed of *pyrophosphate of protoxide of copper, and protoxide of copper and ammonia*, having, when dried over a mixture of chloride of ammonium and caustic lime, the composition $3 (2 CuO, PO_5) + 2 (CuO, 2 NH_3) + 8 HO$.—Sulphate of protoxide of nickel mixed with pyrophosphate of soda, yields *pyrophosphate of protoxide of nickel*, a light green powder, becoming yellow by ignition, and separating in the crystalline state from its solution in aqueous sulphurous acid, when dried at 110° it has the composition $2 NiO, PO_5 + 6 HO$.—*Pyrophosphate of suboxide of mercury*, precipitated from the nitrate by the soda-salt, is a heavy white crystalline powder; when freshly precipitated it is soluble in excess of the soda-salt, a black powder separating on ebullition; when dried at 100° it is not soluble in pyrophosphate of soda, but is blackened by it, when dried at 100° it is $2 Hg_2O, PO_5 + HO$.—Nitrate of protoxide of mercury, mixed with pyrophosphate of soda, yields at first a white precipitate, which becomes yellowish-red on addition of more of the soda-salt; when dried at 100° it is anhydrous *pyrophosphate of protoxide of mercury* $2 HgO, PO_5$.—Nitrate of teroxide of bismuth, mixed with acetic acid, gives with the soda-salt an amorphous white precipitate, becoming crystalline in 24 hours, in which two different kinds of crystals may be distinguished by the microscope. The acid soda-salt dissolves teroxide of bismuth in consider-

(1) An alkaline pyrophosphate added to an excess of nitrate of protoxide of lead yields, according to Gerhardt, a flocculent precipitate, which contains no nitric acid, but is the pure compound $2 PbO, PO_5$.—On addition of nitrate of protoxide of lead to excess of pyrophosphate of soda, the precipitate first formed is stated to dissolve again on application of heat, and to contain varying quantities of alkali, on its becoming permanent.—A definite compound NaO, PbO, PO_5 could be obtained as a granular precipitate, insoluble in water, on boiling the solution of the first precipitate with an excess of pyrophosphate of soda. (Ann. Ch. Phys. [3] XXII, 506).

able quantities; it likewise dissolves a quantity of teroxide of antimony; the solution, on concentration over sulphuric acid, forms a cauliflower-like mass, which, when treated with water, leaves the greater part of the teroxide of antimony undissolved.—Pyrophosphate of protoxide of silver, dissolved in ammonia, and precipitated by alcohol, yields small colourless needles, which lose ammonia on exposure to the air. Pyrophosphates.

Pyrophosphoric Acid; Submodifications of the same.—H. Rose(1) considered it probable that the common phosphate of soda might lose 1 equivalent of basic water, without being converted into the pyrophosphate; experiment showed that nearly the whole of the water was expelled from the salt at 240°, but that it was then almost completely converted into pyrophosphate. H. Rose has accurately investigated the reactions of pyrophosphate of soda. The conversion of a solution of pyrophosphoric acid into common phosphoric acid by an excess of alkali, succeeds, according to Weber, only when the mass evaporated to dryness is perfectly fused; the conversion by acids, is the more complete, the stronger they are, and consequently concentrated sulphuric acid is best adapted for this purpose.—Rose states that pyrophosphoric acid does not precipitate a solution of white of egg. According to his observations, there exists a second modification of pyrophosphoric acid, differing from that which is contained in pyrophosphate of soda; it is obtained by the ignition of the common phosphate; the salts of this modification may be formed in a manner similar to the preparation of the insoluble metaphosphates of Maddrell, (to be presently discussed); namely, by exposing the salts with an excess of phosphoric acid to a temperature which is not sufficiently high to produce metaphosphates. Thus he finds that an insoluble copper-salt may be prepared from nitrate of protoxide of copper and phosphoric acid, the acid of which, separated by means of hydrosulphuric acid in aqueous solution, comports itself like common pyrophosphoric acid.

Double Pyrophosphates.—Persoz(2) has published some researches on the double salts of pyrophosphoric acid(3). The precipitates produced by pyrophosphate of potassa or soda in solutions of other salts, are soluble in an excess of the precipitant; some of them with

(1) Loc. cit. (vide p. 257).

(2) Ann. Ch. Phys. [3] XX, 315; Ann. Ch. Pharm. LXV, 163; J. Pr. Chem. XLI, 353.

(3) The peculiarity of pyrophosphate of soda of forming double salts with facility had previously been noticed by Stromeyer (Schweigger's Jahrb. LVIII, 123).

Double pyrophosphates.

difficulty, (pyrophosphates of baryta, lime, and protoxide of silver); others so easily, that no precipitate is produced with alkaline pyrophosphates in solutions of certain metallic oxides (binoxide of tin and teroxide of gold, f. i.) In these double compounds, the properties of the constituents are frequently found to be much altered; thus, f. i., the solution of pyrophosphate of sesquioxide of iron in pyrophosphate of soda possesses neither the characteristic taste of solutions of sesquioxide of iron nor their colour, (being colourless); nor, indeed, their reactions (hydrosulphuric acid producing no precipitation of sulphur, but merely a brown colouration; sulphide of ammonium, a green colouration, and after some time, a precipitate, which disappears on being washed, the wash-waters assuming a greenish-brown colour). The double pyrophosphates may be prepared in the isolated state, by addition of pyrophosphate of soda to a metallic solution until the precipitate formed ceases to increase, purification by washing, solution in pyrophosphate of soda or potassa, and crystallization by spontaneous evaporation; or still better, by adding pyrophosphate of potassa or soda to a dilute hydrochloric or sulphuric solution of the base which is to form the double salt, until the precipitate first formed has been re-dissolved, (avoiding as far as possible an excess of alkaline pyrophosphate, and promoting the re-solution by agitation); the compounds contained in the solution are then allowed to crystallize out successively, when the double pyrophosphate separates from the solution sooner or later, according to its solubility. Persoz gives the following account of several double salts thus prepared. *Pyrophosphate of magnesia and soda* is very unstable; its solution, left to itself, becomes rapidly turbid.—*Pyrophosphate of sesquioxide of uranium and soda* is of a pure yellow colour, and so easily soluble, that its solution may be concentrated to the consistency of a thick syrup without crystallization; neither hydrosulphuric acid nor sulphide of ammonium decomposes the solution. This is the case likewise with a solution of *pyrophosphate of sesquioxide of chromium and soda,* which has the colour of sulphate of protoxide of nickel, and from which no crystals could be obtained.—*Pyrophosphate of alumina and soda* is colourless and easily soluble in water; the solution, when evaporated to a certain point becomes turbid, depositing pyrophosphate of alumina.—*Pyrophosphate of sesquioxide of iron and soda* is a colourless and easily soluble compound; its solution may be evaporated to a syrupy consistency, when it undergoes a decomposition similar to that of the alumina-compound; (respecting the reactions of this salt, *v. supra*); its

composition is 2 Fe_2O_3, 3 PO_5 + 2 (2NaO, PO_5) + x HO(1).—*Pyrophosphate of protoxide of iron and soda* exists in solution only, and decomposes on exposure to the air; sulphide of ammonium produces immediately a perfect precipitation.—*Pyrophosphate of protoxide of copper and soda* crystallizes in two different ratios of combination, 2 CuO, PO_5 + 2 NaO, PO_5 + 12 HO and 2 CuO, PO_5 + 3 (2 NaO, PO_5) + 24 HO; both compounds are of a sky-blue colour(2). Only minute quantities of crystals of *pyrophosphate of protoxide of copper and potassa* were obtained on account of its solubility.—This compound also exists most likely in different ratios of combination. Neither zinc nor iron produce a turbidity in solutions of the double salts of protoxide of copper with soda and potassa; the former is coated with a slight film of copper, the latter, only after some days, with microscopic crystals of that metal.—A solution of terchloride of gold mixed with pyrophosphate of soda remains clear, the yellow colour of the terchloride of gold disappearing on application of heat; alcohol removes chloride of sodium from the mixture. When carefully protected from light and organic matter, chloride of sodium and pyrophosphate of soda (which had been added in excess) are gradually deposited, while a syrupy fluid remains, which probably contains the compound 2 AuO_3, 3 PO_5 + 2 (2 NaO, PO_5) + x HO.—Persoz intends describing, at some future period, the properties of the double compounds containing the oxides of bismuth, lead, cadmium, mercury, tin, palladium, platinum, nickel, cobalt, beryllium,

Double pyrophosphates.

(1) Fleitmann and Henneberg, who repeated some of the experiments mentioned by Persoz, found the composition of the pyrophosphate of sesquioxide of iron and soda (prepared by boiling pyrophosphate of iron with a quantity of pyrophosphate of soda, insufficient for complete solution, and precipitating by alcohol) to be 2 Fe_2O_3, 3 PO_5 + 2 (2 NaO, PO_5) + 7 HO, when dried at 100°. (Ann. Ch. Pharm. LXV, 387).

(2) Fleitmann and Henneberg make the following statements: if an excess of freshly precipitated pyrophosphate of protoxide of copper be boiled with a solution of pyrophosphate of soda, the fluid, filtered while hot, deposits on cooling white crystalline crusts, which are insoluble in water, and contain 3 (2 CuO, PO_5) + 2 NaO, PO_5 + 7 HO, when dried at 100°. The liquid concentrated in the water-bath yields a faintly blue, crystalline deposit, insoluble in water, which, dried at 100°, is 3 (NaO, CuO, PO_5) + 2 HO. The mother-liquor of this, left exposed to the air, first deposits crystals of pyrophosphate of soda, and afterwards, when concentrated to syrupy consistency, nodular groups of a beautifully blue salt, 2 CuO, PO_5 + 3 (2 NaO, PO_5) + 4 HO, (when dried at 100°). All these salts fuse, when heated to redness; the white insoluble powder, into which a portion of the hydrated protoxide of copper is converted, on being digested with acid pyrophosphate of soda, appears to be of the same composition as the first of the above compounds. (Ann. Ch. Pharm. LXV, 387.)

Double pyrophosphates.

and yttrium. He concludes by calling attention to the necessity, that the existence of these double compounds should be taken into consideration in analytical researches, and that they may also become of medicinal importance, the pyrophosphate of sesquioxide of iron and soda deserving particular attention in this respect.

For details respecting a pyrophosphate, NaO, PbO, PO_5, we refer to page 266, for CaO, NaO, $PO_5 + 4$ HO, to page 264.

Metaphosphoric Acid. Maddrell's Salts.—Gregory(1) had mentioned that the phosphoric acid containing magnesia, as obtained from bones, might be purified by dissolving it after ignition in water, evaporating the solution and exposing the residue for a quarter of, or half an hour to a temperature of 315^0, whereby an insoluble magnesia-salt 2 MgO, 3 PO_5, was formed; the aqueous solution filtered from this yielded pure phosphoric acid. With respect to the purity of this acid, Berzelius(2) remarked that the soda contained in the phosphoric acid prepared from bones had not been taken into account. Maddrell(3) has now found that in proceeding according to Gregory's method, MgO, PO_5 first separates, and then the salt which Gregory had considered as 2 Mg O, 3P O_5, but which Maddrel found to be 3 (MgO, PO_5) + NaO, PO_5; the phosphoric acid separated from these, still contained magnesia and soda. On heating an excess of it with the sulphates of the protoxides of nickel or cobalt, to above 316^0, 6 (NiO, PO_5) + NaO, PO_5 or 6 (CoO, PO_5) + NaO, PO_5 was deposited; the former is a greenish-yellow—the latter a splendid rose-coloured powder; both are insoluble in water and dilute acid, but dissolve in concentrated sulphuric acid.—With pure acid, prepared from phosphorus by means of nitric acid, Maddrell prepared the following salts:—*Metaphosphate of protoxide of nickel*, NiO, PO_5, was obtained by mixing a solution of sulphate of nickel with excess of phosphoric acid, evaporating and heating above 316^0, when it was deposited as a greenish-yellow powder, insoluble in water and dilute acids, soluble in concentrated sulphuric acid.—The *cobalt- and manganese-salts*, CoO, PO_5 and MnO, PO_5, prepared in the same manner, are distinguished from the preceding by their colour only, the former is rose-coloured, the latter white.—The *salt of protoxide of copper*, CuO, PO_5, is formed in the same manner, as a blueish-white powder, from nitrate

(1) Ann. Ch. Pharm. LIV, 94.
(2) Jahresbericht, XXVI, 133.
(3) Phil. Mag. [3] XXX, 322; Chem. Soc. Mem. III, 273; Ann. Ch. Pharm. LXI, 53; . Pr. Chem. XLI, 131.

of protoxide of copper.—The *salt of sesquioxide of iron*, Fe_2O_3, 3 PO_5, as a white powder, from sesquichloride of iron.—The *alumina-salt*, Al_2O_3, 3 PO_5, separated as a white powder, on evaporating a solution of alumina in excess of dilute phosphoric acid and heating above 316°. In the same manner were prepared the *salt of sesquioxide of chromium*, Cr_2O_3, 3 PO_5, of a beautiful green colour, insoluble even in concentrated acids:—the *baryta-*, *strontia-*, *lime-* and *magnesia-salts*, all of them being white powders, whose composition is represented by the general formula MeO, PO_5. After fusing two parts of chlorate of potassa and one of syrupy phosphoric acid, heating strongly and digesting the fused mass with water, the *potassa-salt*, KO, PO_5, remained behind as a white powder, insoluble in water, soluble in dilute and concentrated acids. The *soda-salt*, NaO,PO_5, prepared in the same manner from nitrate of soda, exhibits a similar deportment; it is likewise a white powder insoluble in water. Metaphosphoric acid. Maddrell's salts.

Graham's Metaphosphoric Acid.—This soda-salt then differs in a remarkable manner from Graham's amorphous vitreous metaphosphate of soda, which is deliquescent in the air and contains a modification of metaphosphoric acid, producing with lime, baryta and magnesia, compounds of turpentine consistency(1).

Fleitmann and Henneberg's Salts.—A third modification of monobasic or metaphosphoric acid has been investigated by Fleitmann and Henneberg(2); it is distinguished by forming easily soluble and crystalline compounds with almost all bases.—The point of departure, for the preparation of these compounds, is the soda-salt, which may be obtained in two ways. It forms by exposure of the phosphate of soda and ammonia, (microcosmic salt), to a gradually increasing temperature, when ammonia and water are evolved, a white saline mass being produced, which is perfectly soluble in water, yielding an acid solution. When powdered and exposed to an increased temperature, and constantly stirred, this saline mass loses the remaining water, and with it its acid reaction; if the application of heat be interrupted while the latter reaction is still just perceptible, treatment with water yields an insoluble residue together with a soluble

(1) Graham's metaphosphate of soda gives, according to Fleitmann, a precipitate with nitrate of protoxide of silver, which, when filtered off directly, washed with some cold water, then strongly pressed between blotting-paper and fused, has the composition AgO, PO_5; if the precipitate were left in contact with the liquid overnight, and then washed with cold water, and dried at 100°, its composition was,, according to Weber, 3 AgO, 2 PO_5 + HO (H. Rose, loc. cit. vide p. 257).

(2) Ann. Ch. Pharm. LXV, 304; Gerhardt and Laurent's Compt. Rend. des Trav. Chim. 1849, 12.

Fleitmann and Henneberg's salts.

portion, which may be crystallized by evaporation at about 30°, but not by allowing a hot saturated solution to cool. The other method of preparing it consists in slowly cooling metaphosphate of soda, Graham's salt, formed by the ignition and fusion of phosphate of soda and ammonia, or of the residue obtained by the former method, when a crystalline mass is produced, separating upon treatment with a moderate excess of warm water into two liquid layers, the larger of which may be made to crystallize. The crystals of the *soda-salt*, obtained by one of these methods, appear to belong to the triclinometric system, they dissolve in 4·5 times their weight of water, imparting to it a cooling, purely saline taste; the cold aqueous solution may be kept for a long time without decomposition; on boiling it, acid reaction and decomposition ensue; the salt is quite insoluble in alcohol, and difficultly soluble in very dilute spirit. The formula of the crystals is NaO, PO_5, + 4 HO; dessicated over sulphuric acid or in the water-bath, the greater part of the water is lost.—If a concentrated solution of the soda-salt be mixed with much nitrate of protoxide of silver (in employing a small quantity an admixture of soda-salt is inevitable), the *silver-salt* gradually crystallizes out in beautiful transparent crystals, belonging apparently to the monoclinometric system, and having the composition 3 (AgO, PO_5) + 2 HO(1).—The *lead-salt*, crystallized in the same manner, is PbO, PO_5 + HO.—From a mixture of chloride of barium and soda-salt, in which the former predominates, the *baryta-salt* BaO, PO_5 + 2 HO crystallizes in oblique rhombic prisms; if the soda-salt be present in excess, crystals of a soluble double-salt 2 (BaO, PO_5) + NaO, PO_5 + 8 HO is obtained in stellated tufts (5 HO escape at 100°). Double salts may be obtained with protoxide of zinc and lime, also containing for 1 equivalent of soda two of the other base.—Henneberg and Fleitmann state, moreover, that the salts of lime and strontia are remarkable for the beauty with which they crystallize, while the compounds of magnesia, protoxides of zinc, manganese and cobalt do not crystallize so well.

Rose's fourth Submodification of Metaphosphoric Acid.—H. Rose(2) has given a complete comparison of the properties and reactions of

(1) The acid contained in the silver-salt may, according to Fleitmann, be easily isolated by hydrosulphuric acid, and then affords, on saturation with carbonate of soda, the original soda-salt; on neutralization by ammonia and on addition of nitrate of silver the crystallized silver-salt is again obtained. (H. Rose, loc. cit. p. 257).

(2) Loc. cit. p. 257.

the three submodifications of metaphosphoric acid (in Graham's, Maddrell's, and Fleitmann and Hennenberg's salts) discussed above—if this name be retained for the acid, the salts of which contain 1 equivalent of base to 1 equivalent of acid; he considers it probable that the acid obtained by combustion of phosphorus, to which the property of producing a large precipitate in a solution of chloride of barium is peculiar, may be distinguished as a fourth submodification. All the submodifications of metaphosphoric acid (as also their soluble salts on addition of acetic acid) precipitate a solution of white of egg; this property is not possessed by pyrophosphoric acid, although lately assigned to it by Berzelius. On heating a concentrated solution of common phosphoric acid until it commences to volatilize, metaphosphoric acid is produced, which gives a copious precipitate with chloride of barium; by a rapid application of heat, however, an acid may be obtained, which is not thrown down by chloride of barium.—Weber has confirmed Rose's former statement, that fused phosphoric acid contains rather less water than corresponds with the formula $PO_5 + HO$; a portion exposed for a considerable time to a temperature at which it commenced to volatilize, contained 10·2 per cent. of water. Rose's fourth submodification of metaphosphoric acid.

Blumenau(1) has called attention to a peculiar colouration, appearing on heating and fusing phosphoric acid, prepared from bones, and purified by hydrosulphuric acid, alcohol, and sulphuric acid; he ascribes this colour to the formation of ferric or permanganic acids, or of both.

Other new Modifications of Phosphoric Acid.—The amount of water in many of their salts, and also the composition of the double-salts, induced Fleitmann and Henneberg to assume in these salts the existence of 3 equivalents of fixed base, and 3 equivalents of phosphoric acid. They discuss Graham's view of the different modifications of phosphoric acid, and agree with Liebig, in regarding the composition of the different phosphates in such a light, as to compare quantities of the various salts containing an equal amount of base, as illustrated by the following formulæ (MO representing 1 equivalent of base):

$$6\,MO + 2\,PO_5 \quad 6\,MO + 3\,PO_5 \;\ldots\ldots\; 6\,MO + 6\,PO_5$$



when $6\,MO + 2\,PO_5$ represents the common phosphates, $6\,MO + 3\,PO_5$ the pyrophosphates, and $6\,MO + 6\,PO_5$ the metaphosphates, the transition of one class into the subsequent one being considered

(1) Ann. Ch. Pharm. LXVII, 117.

Other new modifications of phosphoric acid.

as dependent on the assimilation of phosphoric acid. They have endeavoured to fill up the intervals in the above series, by preparing the salts $6\ MO + 4\ PO_5$, and $6\ MO + 5\ PO_5$.

They first prepared the soda-salts by fusing together the compounds $6\ NaO, 2\ PO_5$ or $6\ NaO, 3\ PO_5$ with $6\ NaO, 6\ PO_5$ in the requisite proportions [$2\ (6\ NaO, 3\ PO_5) + (6\ NaO, 6\ PO_5) = 18\ NaO, 12\ PO_5 = 3\ (6\ NaO, 4\ PO_5)$, or $(6\ NaO, 2\ PO_5) + (6\ NaO, 6\ PO_5) = 12\ NaO, 8\ PO_5 = 2\ (6\ NaO, 4\ PO_5)$]. 76·87 parts of Graham's metaphosphate of soda and 100 of anhydrous pyrophosphate, or 187·27 parts of metaphosphate of soda and 100 of the compound $3\ NaO, PO_5$, powdered and very intimately mixed, are fused for a considerable period; on cooling, the mass solidifies with crystalline texture. An excess of the finely powdered salt is digested with hot water, the fluid filtered off, and allowed to crystallize over sulphuric acid, or by exposure to the atmosphere. Crystallization often ensues only after 12 to 24 hours, when a granular crystalline mass is deposited, exhibiting small delicate plates under the microscope. The mother-liquor being drained off, the crystals are washed with some cold water, and dried between bibulous paper. The soda-salt, thus prepared, gave on analysis results agreeing with the formula $6\ NaO, 4\ PO_5$, and a quantity of water oscillating between 7·4 and 8·9 per-cent; it is soluble in about 2 parts of cold water; the solution has a slightly alkaline reaction, decomposition, however, soon ensues (with the formation of other phosphates), an acid reaction becoming manifest at the same time. This decomposition likewise takes place rapidly on treatment with acetic acid, so that by solution therein, and precipitation by alcohol, the acid salt $4\ NaO, 2\ HO, 4\ PO_5$ sought for, could not be obtained. This is, however, the composition of the mass obtained by drying the acid pyrophosphate of soda at 220^0; yet a solution of this salt gave with solution of silver a precipitate of pyrophosphate of silver.—By precipitating a solution of $6\ NaO, 4\ PO_5$ with a solution of silver, (unless employed in excess, the precipitate contains an admixture of common phosphate of silver) a silver-salt $6\ AgO, 4\ PO_5$ was obtained, (nearly anhydrous when dried at 100^0, and of a very low fusing point); sulphate of magnesia yielded with the soda-salt a precipitate of the composition $6\ MgO, 4\ PO_5$ when ignited; with chloride of barium and chloride of calcium, the corresponding salts $6\ BaO, 4\ PO_5$ and $6\ CaO, 4\ PO_5$; the three latter compounds being infusible, and losing by too powerful ignition their solubility in acids.—Fleitmann and Henneberg propose for the acid contained in these salts the name of *sesquiphosphoric acid* because they exhibit the same mode of

composition as the salts termed by Berzelius sesquiphosphates. A characteristic distinction of this acid could not be found; in its reaction it stands between meta- and pyrophosphoric acids. It is, however, distinguished from the former by the insolubility of the magnesia-compound, from the latter by the solubility of the silver-salt in a large excess of the soda-salt. Other new modifications of phosphoric acid.

The soda-salt 6 NaO, 5 PO_5 was obtained by fusing together 2 (6NaO, 6 PO_5) + (6 NaO, 3 PO_5) [= 18 NaO, 15 PO_5 = 3 (6 NaO, 5 PO_5], *i. e.*, 307·5 parts of metaphosphate, and 100 of pyrophosphate of soda; thus prepared, it forms a vitreous mass, crystallizing with more difficulty than the preceding soda-compound. The precipitate by nitrate of protoxide of silver is easily soluble in excess of the soda-salt; when fused it was found to contain 6 AgO, 5 PO_5.

Sulphophosphoric Acid. — According to Wurtz(1), bisulphoterchloride of phosphorus, when heated in the water-bath, with an excess of moderately concentrated soda-solution, yields on cooling a solid mixture of the soda-salt of an acid containing phosphorus and sulphur(2), with chloride of sodium ($PCl_3\ S_2 + 6NaO = PS_2\ O_3$, $3NaO + 3NaCl$). The sulphophosphate may be purified by washing with a little cold water, and recrystallization. The crystals are small thin plates, belonging, according to Provostaye(3), to the hexagonal system, and form, by the predominating terminal planes, a rhombohedron R, and the first more obtuse rhombohedron — ½ R. For R the principal axis = 1·92, the angle of the lateral edge = 104° 20′. The crystals are insoluble in alcohol, easily soluble in boiling water, and efflorescent in the air. They contain 3 NaO, $PS_2\ O_3 + 24$ HO, corresponding to the soda-salt of common phosphoric acid, 3 NaO, $PO_5 + 24$ HO, with which they are not however isomorphous. The solution has a strongly alkaline reaction; chlorine, bromine, and iodine decompose it immediately, separating the sulphur, and seizing a portion of the sodium, while a phosphate is produced (3 NaO, $PS_2\ O_3 + 2\ Cl = NaO, PO_5 + 2\ Na\ Cl + S_2$); nitric acid, even when dilute, acts in a similar manner. Acids, not being oxidizing agents, however weak they may be, separate the sulphophosphoric acid, which at once decomposes into hydrosulphuric and phosphoric

(1) Compt. Rend. XXIV, 288; Ann. Ch. Phys. [3] XX, 472; Ann. Ch. Pharm. LXIV, 245; J. Pr. Chem. XLII, 209.

(2) Cloëz has subsequently called attention to the formation of this acid (Compt. Rend. XXIV, 389).

(3) Ann. Ch. Phys. [3] XX, 482; Compt. Rend. XXIV, 358.

Sulpho-phospho-ric acid. PS_2O_3.

acids ($3HO, PS_2O_3 + 2HO = 3HO, PO_5 + 2HS$). Sulphophosphate of potassa could not be obtained pure; it is very soluble in water, and crystallizes only with difficulty. The lime-, baryta-, and strontia-salts are insoluble in water, as likewise the salts of the protoxides of cobalt and nickel, the latter blacken on boiling. The salt of sesquioxide of iron is obtained as a gelatinous dark red precipitate not changed by boiling. The lead-salt is white at the moment of precipitation, but becomes black after a few hours (and the liquid, acid), sulphide of lead and phosphate of protoxide of lead being produced. The copper-salt decomposes still more easily. The silver- and mercury-salts do not exist; on mixing the soda-salt with nitrate of protoxide of silver, sulphide of silver is immediately formed.

Hydride of Phosphorus. — An appropriate arrangement for the evolution of phosphoretted hydrogen has been described by Knop(1); it allows the disengagement of this gas to be interrupted at pleasure.

Pentachloride of Phosphorus.—Cahours(2) has investigated the action of pentachloride of phosphorus on various organic substances; the results obtained will be described hereafter (comp. anisic acid, benzoic acid, benzilic acid, cinnamic acid, nitranisic acid, nitrobenzoic acid, oil of bitter almonds, Roman cumin oil, cinnamon oil).

Mitscherlich had found the density of vapour of PCl_5 to be 4·85 at 185°, which shows that 1 equivalent of PCl_5 occupies 6 volumes, the volume of O = 1. This condensation in the state of vapour being an isolated case, Cahours(3) has made some experiments on the subject. It is known, that for many organic substances the relation of the specific gravity of their vapours to that of the air differs considerably, according to the temperature, becoming constant only at temperatures far beyond the boiling point; for pentachloride of phosphorus he found the specific gravity:

at 182° = 5·078	at 230° = 4·302	at 288° = 3·67	at 327° = 3·656
190 = 4·987	250 = 3·991	289 = 3·69	336 = 3·656
200 = 4·851	274 = 3·840	300 = 3·654	

Hence the equivalent of PCl_5 occupies 8 volumes, (an assumption on which the specific gravity of the vapour is found by calculation to be 3·61). This condensation is likewise uncommon, and Cahours,

(1) Pharm. Centr. 1848, 649.

(2) Ann. Ch. Phys. [3] XXIII, 327; J. Pr. Chem. XLV, 129; (in abstr.) Ann. Ch. Pharm. LXX, 39; J. Pharm. [3] XIV, 220.

(3) Ann. Ch. Phys. [3] XX, 369; J. Pr. Chem. XLI, 368.

hence, is of opinion that PCl_5 should be considered as consisting of PCl_3 and Cl_2, which constituents have, in the gaseous state, combined in equal volumes without condensation. Penta-chloride of phosphorus.

Bisulpho-terchloride of Phosphorus.—For the bisulpho-terchloride of phosphorus ($PS_2\ Cl_3$), which boils, according to Cahours, at between 126 and 127^0, he found the density of the vapour to be,

5·963 at 168^0; 5·879 at 244^0; 5·878 at 298^0;

corresponding to a condensation of 4 volumes. Cahours regards this body as PCl_3, S_2.

Binoxi-terchloride of Phosphorus.—The same chemist found the density of vapour of binoxi-terchloride of phosphorus ($PO_2\ Cl_3$, boiling point 109^0, *vide infra*,) to be,

5·334 at 151^0; 5·298 at 215^0; 5·295 at 275^0,

corresponding to a condensation of 4 volumes; he regards this compound as PCl_3, O_2. His view as to the constitution of all these combinations is chiefly based upon some observations made respecting PCl_5; in addition to what has been stated above, it rests particularly on the fact of hydrosulphuric acid or aqueous vapour eliminating only two equivalents of chlorine, which appears to indicate that the residue, PCl_3, must be considered as a proximate constituent of this compound.

Binoxi-terchloride of phosphorus was discovered by Wurtz(1), who found that pentachloride of phosphorus, placed in a vessel, together with a small tube containing water, and thus continually exposed to the action of the moist air, forms hydrochloric acid and binoxi-terchloride $PCl_3\ O_2$ ($PCl_5 + 2\ HO = PCl_3\ O_2 + 2\ HCl$). After the decomposition of the pentachloride, the product is distilled; the portion passing over first contains hydrochloric acid, the new compound distilling over at 110^0. It is a colourless liquid, of high refractive power; its odour recalls that of the terchloride of phosphorus (PCl_3). The specific gravity is 1·7 at 12^0, its boil. p. 110^0. Wurtz found the density of its vapour=5·40, 1 equivalent in the state of vapour occupying 4 volumes. It forms white fumes in contact with the air; when in contact with water it dissolves with the formation of hydrochloric and phosphoric acids(2).

(1) Loc. cit. p. 275.

(2) Cahours obtained the binoxi-terchloride of phosphorus by the action of pentachloride of phosphorus ($P\ Cl_5$) on hydride of benzoyl (oil of bitter almonds). The portion of the distillate passing over in the rectification, between 108^0 and 112^0, consisted chiefly of this compound. He found the boiling-point likewise at about 110^0, the spec. grav. = 1·673 at 14^0, the density of vapour = 5·372 at 211^0 (compare other experiments by him p. 276). (Ann. Ch. Phys. [3] XXIII, 329).

Binoxi-terchloride of phosphorus.

Wurtz has given the following synopsis of substances belonging, in his opinion, to the same type:

Pentachloride of phosphorus . .	$P\,Cl_5$	Phosphoric acid	PO_5, 3 HO
Bisulpho-terchloride of phos. .	$P\,Cl_3\,S_2$	Sulphophosphoric acid .	$PO_3\,S_2$, 3 HO
Pentasulphide of phos. . . .	$P\,S_5$	Phosphorous acid . . .	$PO_4\,H$, 2 HO
Binoxi-terchloride of phos. . .	$P\,Cl_3\,O_2$	Hypophosphorous acid .	$PO_3\,H_2$, HO
Binamido-terchloride of phos.	[illegible]	[illegible]	

Attempts to prepare the combinations $PCl_3\,Br_2$, $PCl_3\,I_2$, $PCl_3\,Cy_2$, were unsuccessful.

Sulphur.—Deville(1) has determined the specific gravity of sulphur in its different states. He found (water at its maximum density being = 1) the specific gravity of the rhombic modification to be 2·070 when native, and 2·063 when crystallized from bisulphide of carbon. The specific gravity of the monoclinometric modification, immediately after its passage from the fused into the crystalline state, was 1·958; it increased gradually after eight months to 2·050. Amorphous sulphur, immediately after preparation, showed a specific gravity, of 1·919 and 1·928, which increased gradually in eleven months to 2·051 and 2·061. These experiments confirm the principal points of those made at a former period by Marchand and Scheerer.

Pasteur(2) has observed that sulphur, when crystallizing from bisulphide of carbon, is capable also at the ordinary temperature, of assuming the monoclinometric form, which had been formerly observed only in sulphur solidifying after fusion.

Deville(3) believes that the deposition of monoclinometric crystals of sulphur from its solution in bisulphide of carbon depends upon the presence of *viscid* sulphur in the solution, and that the reddish colour of the crystals thus obtained is due to the same cause. He farther adds, that bisulphide of carbon at 12° dissolves 0·35 of its own weight of sulphur. Rhombic sulphur (whether natural or artificial) is stated to dissolve entirely in bisulphide of carbon, without residue, whilst monoclinometric (freshly prepared or already transformed) leaves a very light whitish residue, never exceeding 0·03 of the original weight; sulphur quickly cooled (soft sulphur or flowers of sulphur) left a residue of 0·11 to 0·35 of the original weight.

According to Schrötter(3), amorphous sulphur is insoluble in

(1) Compt. Rend. XXV, 857.
(2) Compt. Rend. XXVI, 48; Ann. Ch. Phys. [3] XXIV, 459; Pogg. Ann. LXXIV, 94; J. Pr. Chem. XLIV, 120; Ann. Ch. Pharm. LXVIII, 228.
(3) Compt. Rend. XXVI, 117.
(4) Wien. Acad. Ber. 1848, II, 200.

bisulphide of carbon; in order to obtain a product rich in this amorphous modification, sulphur was exposed for 68 hours to a temperature of 360°, and then rapidly cooled.

Hyposulphurous acid.

Hyposulphurous Acid.—Jacquelain(1) has briefly stated that sulphurous acid and sulphur can unite directly in their nascent state to form hyposulphurous acid; the latter is said to be produced in the presence of water by the action of sulphurous and hydrosulphuric acids, (in this case, pentathionic acid is formed, *vide infra*). According to Jacquelain's statement, hyposulphite of baryta can be prepared in quantity by mixing a solution of sulphide of barium with excess of a solution of sulphurous acid, heating to 50°, filtering, &c. &c., or by passing a current of sulphurous acid gas into a solution of baryta heated to 50°, and containing sulphur in suspension.

F. Kessler(2) has accurately investigated some of the salts of hyposulphurous acid. According to former statements, the *potassa-salt* crystallizes with water in four proportions (Rammelsberg analyzed a salt $3\,(KO,S_2O_2)+HO$; Döpping obtained a salt by decomposing pentasulphide of potassium with chromate of potassa, crystallizing sometimes in prisms of the composition $KO,\,S_2O_2+HO$, at other times in rhombic pyramids of the composition $2\,(KO,\,S_2O_2)+3\,HO$; Plessy asserts, that by boiling sulphur with sulphite of potassa, he formed $KO,\,S_2O_2+2\,HO$). Kessler has obtained, by the gradual addition of a hot solution of bichromate of potassa to a hot solution of pentasulphide of potassium, and evaporation of the liquid at 30°, thin four-sided prisms of the composition $3\,(KO,\,S_2O_2)+HO$; the mother-liquor, when strongly agitated, yielded small granular crystals, which, when dissolved in warm water, deposited on cooling rhombic pyramids of the composition $3\,(KO,\,S_2O_2)+5\,HO$, which agrees with the results obtained in Döpping's analysis. Hyposulphite of potassa, obtained by boiling sulphite of potassa with sulphur, exhibited the same phenomena respecting the formation of two kinds of crystals. A double salt of *hyposulphite of potassa and cyanide of mercury* $KO,\,S_2O_2+Hg\,Cy$ was obtained only once in the form of large four-sided prisms, by the addition of alcohol to a solution of equal equivalents of both salts and concentration of the mother-ley in vacuo. *Hyposulphite of strontia* was obtained most easily by mixing concentrated hot solutions of equal equivalents of nitrate of strontia and hyposulphite of soda,

(1) Ann. Ch. Phys. [3] XXI, 110; J. Pr. Chem. XLII, 388.
(2) Pogg. Ann. LXXIV, 274; Ann. Ch. Pharm. LXVIII, 231, (in abstr.).

Hyposulphurous acid.

when this salt crystallized out on cooling; SrO, S_2O_2 + HO separated in small prismatic crystals on evaporating a solution at or above 50°.—The *double salt of magnesia and potassa* was obtained by Kessler on mixing hot solutions of equal equivalents of hyposulphite of potassa and sulphate of magnesia; the sulphate crystallized from the liquid on cooling, and the double hyposulphite on evaporating the mother-ley at a low temperature. He obtained the corresponding ammonia double salt, MgO, $S_2O_2 + NH_4O, S_2O_2$ + 6 HO, by decomposing the double sulphate with hyposulphite of strontia; the concentrated solution becoming turbid when warmed, and depositing, only at temperatures below 0°, crystals of the double salt, which readily deliquesce.

Sulphurous Acid.—The solid combination of sulphurous acid with water has been more minutely investigated by Pierre(1). The crystalline body, which was obtained by passing sulphurous acid and aqueous vapour into a vessel cooled to —6° or —8° and to which ice possibly might adhere, contained about 24·2 of acid to 75·8 of water; crystals which separated at about 0° from a saturated solution of sulphurous acid contained 25·1 to 26·1 percent of acid; the same fused and recrystallized contained 27·9 sulphurous acid, corresponding nearly to the formula SO_2 + 9HO, which requires 28·3 of acid to 71·7 of water. —The crystals appear to be monoclinometric, they are heavier than water, which at 10° dissolves about half its weight of them; freed from the liquid they may be exposed to the air for some time without perceptibly absorbing oxygen; at a slight increase of temperature they fuse and disengage sulphurous acid.— Pierre has found also that liquid sulphurous acid, when brought into contact with water, at a temperature lower than its boiling point, does not combine with it, some of the acid only being taken up by the water with the formation of the compound already described; also when heated in sealed tubes with water to + 12°, liquid sulphurous acid does not combine with it.

Döpping(2) appears to have obtained the same compound, though not free from adhering moisture, by passing a current of sulphurous acid gas into water surrounded with ice, when a crystalline body separated, which fused between —1° and —2°. Döpping's analysis of these crystals gave 24·0 to 25·6 percent of

(1) Ann. Ch. Phys. [3] XXIII, 416; Compt. Rend. XXVII, 21 (in abstr.); J. Pr. Chem. XLV, 237; Ann. Ch. Pharm. LXVIII, 228.

(2) Petersb. Acad. Bull. VII, 100; J. Pr. Chem. XLIV, 255.

sulphurous acid; an error of calculation(1) led him to believe that they contained equal equivalents of sulphurous acid and water. Döpping supposes that there exists another compound which crystallizes at —6° to —7° from the mother-liquor of the former; it could not be more accurately examined. Sulphurous acid.

J. S. Muspratt(2) has again investigated the composition of several sulphites, some discrepancies having existed between his former data and those of Rammelsberg(3), particularly with respect to the water(4) which they contain. For the *soda-salt* crystallized over sulphuric acid, he again found $NaO, SO_2, + 10\ HO$ (according to Rammelsberg it contains only 7 HO). By saturating a strong solution of caustic ammonia with sulphurous acid, until the odour of both compounds had disappeared, and adding alcohol, he obtained an *ammonia-salt*, to which, when dried over sulphuric acid, he assigns the formula $2\,(NH_4O, SO_2) + NH_3 + 3HO$. Crystallized *sulphite of protoxide of iron* has, according to his results, which agree with those of Fordos and Gélis, the composition $FeO, SO_2 + 3HO$; the yellowish crystalline precipitate, which is produced by potassa in a solution of freshly precipitated sesquioxide of iron in aqueous sulphurous acid, is $Fe_2O_3, SO_2 + 2(KO, SO_2) + 5\,HO$. From the solution of carbonate of protoxide of nickel in water which was subjected to a continuous stream of sulphurous acid, he again obtained crystals of a salt of *protoxide of nickel* agreeing in composition with that formerly given by him, namely, $NiO, SO_2 + 4HO$. If the precipitate, which is produced by alcohol in a solution of carbonate of protoxide of cadmium in aqueous sulphurous acid, be allowed to remain for several days in contact with the liquid, a crystalline *salt of cadmium* is formed, $CdO, SO_2 + 2HO$. As to the red *copper-salt* which is produced by the action of sulphurous acid on protoxide of copper suspended in water, and to which Rammelsberg had assigned the formula $CuO, SO_2 + Cu_2O, SO_2 + HO$. Muspratt adheres to his formula $Cu_2O, SO_2 + HO$; he states that boiling water removes from it the half of its amount of sulphurous acid. A *double salt* of *sulphite of suboxide of copper* and *sulphite of soda* was prepared by mixing a saturated solution of sulphite of protoxide of copper and sulphite of soda, addition of absolute alcohol and evaporation *in vacuo* of the dark red fluid which separated;

(1) Compare Arch Ph. Nat. IX, 222; Ann. Ch. Pharm. LXVIII, 230.
(2) Phil. Mag. [3] XXX, 414; Chem. Soc. Mem. III, 292; J. Pr. Chem. XLI, 211; Ann. Ch. Pharm. LXIV, 240.
(3) Ann. Ch. Pharm. L, 259.
(4) Pogg. Ann. LXVII, 245, 391.

Sulphuric acid.

the fine yellow crystals, which deposited, had the composition Cu_2O, $SO_2 + 5 (NaO, SO_2) + 38HO$.

Sulphuric Acid.—Barreswil(1) has found, that by distilling hydrated sulphuric acid with anhydrous phosphoric acid, anhydrous sulphuric acid is obtained in the receiver. Evans(2) recommends this method for the preparation of the latter body.

In order to prevent the bumping in the rectification of sulphuric acid, Lembert(3) has recommended the introduction of pieces of quartzite, and Redwood(4) that of pieces of rock crystal into the retort. Rieckher(5) has communicated his experience with regard to the rectification of this acid.—Hayes(6) recommends the purification of crude sulphuric acid, by heating it with a little nitre and then with sulphate of ammonia and concentrating until the specific gravity is 1·78. After allowing the liquid partly to crystallize, it has to be rectified.

Mixtures of Sulphuric Acid and Water.—Bineau(7) has ascertained the spec. grav. of mixtures of hydrated sulphuric acid and water. He determined (for 0^0) the spec. grav. of a number of mixtures in different proportions, the composition of which he established analytically, and then sought by interpolation the spec. grav. of mixtures in simple ratios; he farther ascertained the alteration of the spec. grav. by a change of temperature. In this manner the following table was constructed, the first column of which contains the percentage by weight of sulphuric acid in aqueous acid, the second the spec. grav. at 15^0, the third the appropriate indications of Baumé's areometer (for the same temperature), the latter, under the assumption that 66^0 of Baumé correspond to the spec. grav. 1·842.

5	1·032	4^0·5	30	1·223	28^0·2	55	1·448	44^0·7	80	1·734	61^0·1
10	1·068	9·2	35	1·264	30·1	60	1·501	48·2	85	1·786	63·5
15	1·106	13·9	40	1·306	33·8	65	1·557	51·6	90	1·822	65·1
20	1·144	18·1	45	1·351	37·5	70	1·615	55·0	95	1·838	65·8
25	1·182	22·2	50	1·398	41·1	75	1·675	58·2	100	1·842	66·0

Bineau states, that he was not able to obtain the pure hydrate of

(1) Compt. Rend. XXV, 30; Phil. Mag. [3] XXXI, 314; J. Pr. Chem. XLII, 384.
(2) Pharm. J. Trans. VIII, 127; J. Chim. Méd. [3] V, 9.
(3) J. Pharm. [3] XII, 166; J. Pr. Chem. XLII, 341.
(4) Pharm. J. Trans. VIII, 82.
(5) Jahrb. Pr. Pharm. XV, 78.
(6) Sill. Am. J. [2] VI, 113.
(7) Ann. Ch. Phys. [3] XXIV, 337; J. Pharm. [3] XV, 30; Ann. Ch. Pharm. LXVIII, 240; J. Pr. Chem. XLVI, 98.

sulphuric acid by concentrating the dilute acid; the product contained always, at the least, 1 percent more water than the formula required. He mentions, that according to his experiments, the greatest condensation attending the mixing of hydrated sulphuric acid and water did not correspond to a mixture in stœchiometrical proportions, (it had been formerly asserted, that the maximum condensation took place with the mixture SO_3, HO + 2 HO or SO_3 + 3 HO). Mixtures of sulphuric acid and water.

Decomposition of Sulphates. — Bastick(1) communicates, that well-water containing gypsum in solution, having been shaken with an etherial oil and allowed to stand in a close vessel for three weeks, became saturated with hydrosulphuric acid, whilst the oil disappeared and carbonate of lime was deposited.

A. d'Heureuse(2) has published some researches on the behaviour of iron and zinc with sulphuric acid and its combinations.—Iron, exposed to the vapour of anhydrous sulphuric acid at a high temperature, by placing a crucible filled with iron wire into one containing sulphate of bismuth, which was closed and subjected for half an hour to a red heat, was converted into a fused blistered mass of a metallic grey colour and a bronze-like fracture; according to d'Heureuse 4 SO_3 give with 13 Fe a mixture of 3 (FeO, Fe_2O_3) and 4 FeS; he states, that a small portion of the sulphuric acid was, however, decomposed by the heat into oxygen and sulphurous acid, and that from such a mixture iron absorbed chiefly oxygen, so that the mass formed was somewhat richer in oxygen than the explanation given would lead us to expect. Zinc, treated in the same manner, was converted into a greenish-yellow powder, a mixture of protoxide and protosulphide of zinc; $SO_3 + 4\ Zn = 3\ ZnO + ZnS$.—Sulphate of potassa exposed for a short time to a moderate red heat with an excess of finely divided iron was entirely decomposed; KO, SO_3 and 3 Fe give KO, Fe_2O_3 and FeS. Water extracts from the blackish porous mass a solution of sulphide of iron in potassa which is brownish-yellow when hot and dark-green when cold; on exposure to the air it is decolorized with deposition of a dark-brown precipitate, sulphide of potassium and a hyposulphite of potassa being produced. On addition of copper, a mass is obtained from which water extracts caustic potassa and hyposulphite of potassa; the solution contains no sulphide of iron. Sulphate of potassa, heated with an excess of zinc, is likewise completely decomposed, (this mixture exhibits, even below a red heat, a beautiful incandescence)

(1) Pharm. J. Trans. VII, 105.
(2) Pogg. Ann. LXXV, 255; Ann. Ch. Pharm. LXVIII, 242 (in abstr.).

Decomposition of sulphates.

and yields a compact mass of a lemon-yellow colour, containing sulphide of potassium; $KO, SO_3 + 4 Zn = KS + 4 ZnO$.—Sulphate of soda behaves in a similar manner both with iron and zinc. Iron or zinc, when heated in a solution of sulphate of ammonia, are dissolved (the iron as protoxide), with disengagement of ammonia. The fused salt acts in the same manner more energetically. By heating rapidly to redness a mixture of sulphate of ammonia and iron, sulphurous acid is evolved after the vapour of the salt has been disengaged; the iron is slightly oxidized and sometimes combined with sulphur.—Sulphate of lime, heated strongly with iron, yields a black-grey mass, of metallic appearance, containing sulphide of calcium, and both proto-sesquioxide and sesquioxide of iron; zinc, heated to redness with sulphate of lime, deflagrates violently, and yields a porous yellowish mass containing lime, and both protoxide and protosulphide of zinc; $CaO, SO_3 + 4 Zn = CaO + 3 ZnO + ZnS$.—Sulphate of baryta behaves in a similar way; it is more easily decomposed by iron than by charcoal, but water extracts the sulphide of barium only incompletely from the mass thus obtained. Chloride of barium is easily obtained by mixing 2 p. of heavy spar and 2 of iron with a solution of 1 of chloride of calcium, evaporating, and heating to redness for a short time in an iron crucible. The mass is poured out while still hot, pulverized after cooling, and extracted with hot water, a little hydrochloric acid being added, in order to decompose a trace of sulphide of calcium which is dissolved, and evaporated to crystallization. In the same manner chloride of strontium can be prepared from celestine; this mineral requires, however, a higher temperature for decomposition than either the lime- or baryta-salt, and the mass produced yields a larger quantity of sulphide of strontium, but not the whole when treated with water. —On heating sulphate of magnesia with iron, a large quantity of sulphurous acid is given off, while an iron-grey mass remains, which contains no sulphide of magnesium, but consists chiefly of protoxide and sesquioxide together with a trace of sulphide of iron. Zinc gives rise to a similar decomposition, attended by a violent deflagration.—Iron and zinc act only very slightly, if at all, on neutral sulphate of alumina at high temperatures.

Di-, Tri-, Tetra- and Pentathionic Acids.—It is known that several acids have been discovered of late, in which 5 equivalents of oxygen are combined with varying quantities of sulphur. Formerly hyposulphuric acid ($S_2 O_5$), discovered by Welter and Gay Lussac in 1819, was the only acid of this kind with which we were acquainted; in 1841 Langlois found the acid $S_3 O_5$ which is formed by con-

tinuously heating sulphur with bisulphite of potassa; in 1842 Fordos and Gélis discovered the acid S_4O_5, produced by the action of iodine on hyposulphite of soda or baryta; in 1846 Wackenroder assigned the formula S_5O_5 to an acid which he obtained by the mutual action of hydrosulphuric and sulphurous acids in the presence of water. Plessy asserted in 1845 that an acid S_4O_5 is formed by the action of subchloride of sulphur on a solution of sulphurous acid, differing from that of Fordos and Gélis, whilst the chloride of sulphur forms, with the same solution, an acid S_5O_6. Researches relating to these acids (with regard to the nomenclature of which, we concur in the proposition to apply to S_2O_5 the term dithionic acid, to S_3O_5 trithionic acid, to S_4O_5 tetrathionic acid, and to S_5O_5 pentathionic acid) have been published in 1847 and 1848 by Plessy(1), Jacquelain(2), Lenoir(3), Ludwig(4), Fordos and Gélis(5), and F. Kessler(6). Respecting the acids containing more than 5 equivs. of oxygen, Plessy has stated that subchloride of sulphur (S_2 Cl) produces with sulphurous acid and water the acids S_3O_5 and S_4O_5 only, (he admitted the identity of the latter with that discovered by Fordos and Gélis), and that chloride of sulphur, prepared by heating the subchloride in chlorine, when treated with sulphurous acid in excess, forms the same acid, with a smaller amount, however, in addition to the acid S_4O_5, also the acids S_5O_6 and S_5O_7. Fordos and Gélis, who made use of more exact analytical methods, have ascertained that both subchloride and chloride of sulphur give rise to the same sulphur-acids, by their action on water and sulphurous acid, (the co-operation of the latter they found to be altogether unessential), and that a difference is exhibited only in respect to the quantity of sulphur which separates at the commencement of the reaction. They believe that the first result of this reaction is the production of S_5O_5, from which soon separates S_4O_5, and then S_3O_5, along with other products of decomposition. They never found an acid containing more than 5 equivs. of oxygen.

Di-, tri-, tetra- and Penta-thionic acids.

Dithionic Acid.—According to a short statement of Jacquelain,

(1) Ann. Ch. Phys. [3] XX, 162; J. Pr. Chem. XLI, 329; Compt. Rend. XXIV, 198 (in abstr.); Ann. Ch. Pharm. LXIV, 247.

(2) Ann. Ch. Phys. [3] XXI, 110; J. Pr. Chem. XLII, 338.

(3) Ann. Ch. Pharm. LXII, 253; J. Pr. Chem. XLIII, 455 (in abstr.).

(4) Arch. Pharm. [2] LI, 259.

(5) Ann. Ch. Phys. [3] XXII, 66; J. Pr. Chem. XLIII, 456; Compt. Rend. XXV, 623 (in abstr.); Ann. Ch. Pharm. LXIV, 249.

(6) Pogg. Ann. LXXIV, 249; Ann. Ch. Pharm. LXVIII, 233 (in abstr.); Laurent's and Gerhardt's Compt. Rend. des Trav. Chim. 1849, 139.

Dithionic acid. dithionic acid also is gradually produced along with sulphuric in an aqueous solution of sulphurous acid to which the air has only very partial access, (he examined a solution which had been prepared two years previously).

Trithionic Acid.—Kessler obtained trithionic acid in aqueous solution by decomposing the potassa-salt with hydrofluosilicic acid; the liquid, however, could not be concentrated even at 0^0 without disengagemement of sulphuric and sulphurous acids. He confirmed the formula KO, S_3O_5 for the crystallized potassa-salt. He found the formula BaO, $S_3O_5 + 2$ HO for a baryta-salt (dried between filtering-paper), which had been obtained by saturating the aqueous acid with carbonate of baryta and adding a large quantity of absolute alcohol, when the salt was precipitated in brilliant scales; the aqueous solution of this salt is very rapidly decomposed.—He did not confirm the statement of Baumann, that trithionates are formed by digestion of dithionates with sulphur.

Tetrathionic Acid.—According to Kessler tetrathionic acid is best prepared from the lead-salt. In order to obtain this salt, hyposulphite of lead is prepared by mixing a solution of two parts of hyposulphite of soda, dissolved in a large quantity of warm water, with a warm and likewise dilute solution of three parts of acetate of lead; the precipitate, which has been well washed with warm water whilst still moist, is mixed with one of iodine and stirred repeatedly. After some days, the whole is converted into iodide of lead and a solution of tetrathionate of lead, which latter is to be decomposed by sulphuric acid (not by hydrosulphuric acid). Tetrathionate of strontia is obtained by mixing tetrathionic acid with a proper quantity of an aqueous solution of acetate of strontia and addition of alcohol; dried between blotting-paper it contains SrO, $S_4O_5 + 6$ HO. The lead-salt prepared in the same way contains PbO, $S_4O_5 + 2$ HO. Neither the lead-, the soda- nor the copper-salt can be obtained in the crystalline state by evaporating their aqueous solutions. The nickel- and cadmium-salts form deliquescent crystalline masses.

Pentathionic Acid.—Lenoir has found the baryta-salt of this acid to contain BaO, $S_5O_5 + 2$ HO, besides a small amount of alcohol. He prepared it according to the method of Wackenroder, by the reaction of sulphurous on hydrosulphuric acid in the presence of water, and saturation with carbonate of baryta, when transparent square prisms of the salt were deposited on the addition of alcohol. Hence the small quantity of alcohol which Kessler found in the crystals. The aqueous solution of this salt is decomposed by heat. Fordos and Gélis, who obtained this acid (S_5O_5) several times by

the action of chloride of sulphur on an aqueous solution of sulphurous acid, arrived at the same composition; they obtained a salt free from alcohol by precipitating the aqueous solution with ether containing very little alcohol. They call attention to the fact, that the salt containing alcohol can be preserved for a longer time without decomposition than the salt which is free from it.—Ludwig states that pentathionic acid is likewise formed by the action of a warm aqueous solution of sulphurous acid on freshly prepared pentasulphide of hydrogen. Pentathionic acid.

Kessler reminds us that Persoz had formerly obtained pentathionic acid, by decomposing hyposulphite of lead with hydrosulphuric acid, but had mistaken it for hyposulphurous acid.

The same chemist has determined the specific gravity, and the composition of aqueous pentathionic acid; the following are his results:

Spec. grav. at + 22°:	1·233	1·320	1·474	1·506
Percentage of $S_5\,O_5$:	32·1	41·7	56·0	59·7

He has also subjected the reactions of tri-, tetra-, and pentathionic acids, to a comparative examination.

The ready decomposition of the aqueous solution of pentathionate of baryta with deposition of sulphur has been confirmed by Lenoir, Fordos and Gélis, Ludwig and Kessler. Fordos and Gélis found that the crystals which are separated by alcohol at different periods of the decomposition, require less and less chlorine for the complete conversion of the sulphur into sulphuric acid, the farther the decomposition is advanced; the crystals contain at first BaO, $S_5\,O_5$, with BaO, $S_4\,O_5$, then BaO, $S_4\,O_5$ with BaO, $S_3\,O_5$, and at last only the latter salt. Ludwig found that by evaporating pentathionates of potassa and baryta with an excess of pentathionic acid and allowing them to crystallize, salts are obtained which contain 9 equivs. of sulphur and 10 equivs. of oxygen to 2 equivs. of base: $2\,KO, S_9\,O_{10}+HO$ and $2\,BaO, S_9\,O_{10}+6\,HO$ (in the preparation of the latter salt, BaO, $S_4\,O_5+2\,HO$ crystallized out of the mother-liquor.) He considered these salts as compounds of a peculiar tetrapentathionic acid. On adding aqueous pentathionic acid to an alcoholic solution of acetate of potassa, Kessler obtained a precipitate which, when dissolved in water (sulphur remaining behind) and treated with alcohol yielded crystals of KO, $S_4\,O_5$. By mixing aqueous solutions of pentathionic acid and acetate of baryta, and adding alcohol, a precipitate was obtained which, when dissolved in water and reprecipitated by alcohol, was found to yield a salt (when dried

Penta-thionic acid.

between blotting-paper) of the composition $2\,BaO, S_9O_{10}+7\,HO$. Still Kessler does not believe in the existence of tetrapentathionates as peculiar salts, but considers them as mixtures of tetra- and pentathionates, which are, perhaps, capable of crystallizing together in all proportions.

Selenium.—Schaffgotsch(1) has examined the spec. grav. of selenium. Rapidly cooled after fusion, this element gave (for 20°) spec. grav. from 4·276 to 4·286, as a mean 4·282; slowly cooled, 4·796 to 4·805, as a mean 4·801; when precipitated in the state of a finely divided red powder, by means of sulphurous acid from aqueous selenious acid, 4·259; this precipitate, which blackened on heating, gave a spec. grav. of 4·264.

Sacc(2) has made some experiments for the purpose of determining the equivalent of selenium. By converting a known quantity of selenium into selenious acid (by means of nitric acid) and determining the increase in weight, he arrived at the numbers 40·0, 40·5, 39·2, the last of which he considers to be the most correct, because the selenious acid obtained in the two first determinations had an odour of nitric acid. In determining how much selenium was procured by reducing a known weight of selenious acid, he arrived at the numbers 39·2, 39·0, 39·5. He takes 39·2 as the mean. For controlling the above, he determined how much sulphate of baryta and selenium were formed by digesting at a gentle heat a weighed quantity of selenite of baryta with bisulphite of ammonia. A comparison of these results with the numbers calculated according to the equivalent which he had adopted, appeared to him satisfactory, although discrepancies were exhibited amounting to nearly $\frac{2}{100}$ths of the weight. Concordant determinations of the quantities of sulphate of baryta formed by the decomposition of the selenite, led to the equivalent 39·3; the analysis of the silver-salt, conducted in the same way, gave 39·6 and 39·4. These numbers are stated to be somewhat too high, because some metallic silver was mixed with the sulphate of silver. The decomposition of selenite of lead, by means of sulphuric acid, was not complete. He adopted the equivalent 39·3; according to the determination of Berzelius it is 39·5.

Selenite of Soda.—A solution of selenious acid, saturated with carbonate of soda, yielded crystals when evaporated *in vacuo* to the

(1) Berl. Acad. Ber. Nov. 1847; J. Pr. Chem. XLIII, 308; Ann. Ch. Pharm. LXVIII, 247; Instit. 1848, 168.

(2) Ann. Ch. Phys. [3] XXI, 119; J. Pr. Chem. XLII, 329; J. Pharm. [3] XII, 442.

consistency of a syrup. Dried at 90° and analysed, this salt was found to contain 3 equivalents of selenious acid to 2 of soda. Selenite of soda.

Chloride of Selenium.—Sacc(1) has likewise made an analysis of the liquid subchloride of selenium; he acknowledges for this compound the formula Se_2 Cl, found by Berzelius, although his own analyses do not agree with it.

Iodine.—Von der Mark(2) has found iodine in the *Jungermannia albicans L.* Both bromine and iodine have been discovered in Silesian coals, by Duflos(3).—In order to obtain iodine from the most dilute solutions, Persoz(4) recommends to pass sulphurous acid into the liquid until it smells strongly of the gas, to add sulphate of protoxide of copper and bisulphite of soda, when a precipitate of subiodide of copper is immediately formed, which is decomposed in the usual manner.

The presence of iodide of cyanogen in commercial iodine has been observed by Scanlan(5), and by F. Meyer(6).

Iodide of Potassium.—Seleniate of potassa is stated to have been detected in commercial iodide of potassium by Trez(7); the presence of iodate of potassa in iodide of potassium has been discussed by Lepage(8) and Leroy(9); that of bromide of potassium by Moullard(10).

Diesel(11) has made experiments upon the deportment of iodide of potassium with sulphuric acid; he found that iodide of potassium which was perfectly free from sulphide, when acted upon by concentrated sulphuric acid, evolved not only sulphurous acid but likewise hydrosulphuric acid; this, however, did not occur by the action of dilute acid; hydrosulphuric acid was also evolved by the action of hydrochloric acid, containing sulphuric, upon iodide of potassium. Wackenroder(12) corroborates these statements regarding the action of sulphuric acid; according to his observations, sulphurous acid does not apparently decompose iodide of potassium; the smallest admixture of sulphide in iodide of potassium, he states, may be easily detected

(1) Ann. Ch. Phys. [3] XXIII, 124; J. Pr. Chem. XLV, 94.
(2) Arch. Pharm. [2] LI, 154.
(3) Arch. Pharm. [2] XLIX, 29.
(4) J. Pharm. [3] XII, 105; J. Pr. Chem. XLII, 346.
(5) Chem. Soc. Mem. III, 321.
(6) Arch. Pharm. [2] LI, 29.
(7) Phil. Mag. [3] XXXII, 397; J. Chim. Méd. [3] IV, 201.
(8) J. Chim. Méd. [3] IV, 587.
(9) Ibid. [3] IV, 589.
(10) Ibid. [3] III, 591.
(11) Arch. Pharm. [2] XLIX, 272.
(12) Ibid. [2] XLIX, 275.

Iodide of potassium. with protochloride of tin, by the evolution of hydrosulphuric acid.

Bromine.—Poselger(1) has observed that in the distillation of commercial bromine, towards the end of the operation, the boiling point rose to 120°; from the last portion of the distillate bromide of carbon (found 6·7 to 7·1 carbon to 91·8 bromine, calculated 7 to 93), separated on addition of caustic potassa, as a sweet, colourless, aromatic and highly refractive fluid, of a spec. grav. 2·436, boiling at 120°, and not solidifying at —25°. This fluid is incombustible, only slightly soluble in water, but miscible with alcohol, ether and bromine in all proportions; it is not decomposed by strong sulphuric and nitric acids.

Chlorine. Chlorous Acid.—According to de Vry(2), chlorous acid (ClO_3), mixed with carbonic acid, is prepared easily and without danger, by boiling the solution of chloric and tartaric acids, which is obtained after mixing equal equivalents of chlorate of potassa and tartaric acid and crystallization of the double salt of chlorate and tartrate of potassa.

Chloric Acid.—For the preparation of chlorate of baryta, equal equivalents of chlorate of potassa and bitartrate of ammonia (122·6 of the former to 167 of the latter) are recommended by L. Thompson(3) to be dissolved in the smallest possible quantity of boiling water; after the bitartrate of potassa has crystallized out, the fluid is to be mixed with an equal volume of alcohol. The filtered solution of chlorate of ammonia is now decomposed by digestion with freshly precipitated carbonate of baryta and the filtrate allowed to crystallize. Chlorate of strontia and lime may be prepared in a similar manner.

Chloride of Lime.—Mène(4) suggests as an improvement in the preparation of chloride of lime, the repeated treatment of slacked lime with chlorine-water.—Bastick(5) has described the action of chloride of lime upon sugar, starch, cotton-wool, &c.; when free lime is present, formiate of lime is produced, while, if it be absent, carbonic acid is formed. The action upon a solution of sugar is exceedingly violent; chloride of lime containing free lime, forms, with a solution of glue, formiate of lime and ammonia.

(1) Pogg. Ann. LXXI, 297.
(2) Ann. Ch. Pharm. LXI, 248.
(3) Phil. Mag. [3] XXXI, 510; J. Pr. Chem. XLIII, 73; J. Pharm. [3] XIV, 67.
(4) Compt. Rend. XXV, 747.
(5) Pharm. J. Trans. VII, 467; J. Pharm. [3] XIV, 20.

Fluorine. Hydrofluoric Acid — According to Louyet(1) the liquid hydrofluoric acid, which has been considered as anhydrous, still contains water. He states that it requires less base for neutralization than is necessary on the former assumption. By the distillation of fluor-spar with sulphuric acid, previously heated to ebullition, the product being conducted over anhydrous phosphoric acid, no liquid was condensed in the receiver surrounded by a frigorific mixture, the phosphoric acid, however, deliquesced. Louyet concludes that anhydrous hydrofluoric acid is a gaseous body at —12° under ordinary atmospheric pressure. Liquid hydrofluoric acid.

Nitrogen. Protoxide of Nitrogen.—According to Gay Lussac(2) protoxide of nitrogen is evolved in a state of purity by the action of protochloride of tin upon aqua regia; the evolution is most uniform, if crystals of nitre or cylinders of fused nitre are gradually introduced through a wide tube dipping into a solution of protochloride of tin in hydrochloric acid, which is heated in a water-bath.

Dumas(3) has described some properties of liquified protoxide of nitrogen which he had prepared by means of Natterer's apparatus. When slowly evaporating in open vessels, the introduction of small pieces of metal causes a hissing similar to that of red-hot iron in water; mercury immediately solidifies in it; potassium, sulphur, phosphorus, iodine, and carbon float upon it without change. Ignited charcoal is rapidly burned; common sulphuric and nitric acids are readily solidified, as also water, which gives rise to such powerful evaporation that explosions sometimes occur. Alcohol and ether may be mixed with protoxide of nitrogen without being solidified.

Binoxide of Nitrogen.—According to the observations of Pelouze and Gay Lussac(4), binoxide of nitrogen is conveniently prepared in the same manner as the protoxide, by substituting protochloride of iron for protochloride of tin.

Binoxide of Nitrogen and Nitrous Acid.—According to Schönbein(5) nitrites of protoxide of lead and of protoxide of manganese are formed by the action of binoxide of nitrogen upon finely divided binoxides of lead and manganese suspended in water. Binoxide of nitrogen produces with protoxide of silver, under the same circum-

(1) Compt. Rend. XXIV, 434.
(2) Ann. Ch. Phys. [3] XXIII, 229.
(3) Compt. Rend. XXVII, 463; Instit. 1848, 350; J. Pharm. [3] XIV, 411; Ann. Ch. Pharm. LXVIII, 224; J. Pr. Chem. XLVI, 110.
(4) Ann. Ch. Phys. [3] XXIII, 216.
(5) J. Pr. Chem. XLI, 225.

Binoxide of nitrogen and nitrous acid.

stances, nitrite of protoxide of silver, a portion of the metal being reduced; with teroxide of gold, nitric acid and metallic gold; with binoxide of hydrogen, nitric acid; with iodine or bromine, hydriodic or hydrobromic and nitric acids, but only in limited quantity, both products decomposing each other when highly concentrated.—According to Schönbein(1) aqueous solutions of nitrites are converted into nitrates by oxidized water, ozone, bromine and chlorine, and probably also by binoxide of lead and manganese.

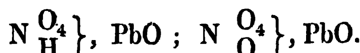
Nitrites.—N. W. Fischer(2) has published observations upon the preparation and qualitative deportment of some nitrites. Nitrite of potassa, forming indistinct and deliquescent crystals, is prepared by fusing nitre, dissolving the mass in water, allowing the nitre to crystallize out, neutralizing with dilute acetic acid, adding spirit of wine, and crystallizing the aqueous layer which is formed *in vacuo*. Nitrite of soda prepared in a similar manner deliquesces less readily. The baryta-salt (obtained by fusing the nitrate, precipitating the free baryta by carbonic acid and the nitrate by addition of alcohol to a concentrated aqueous solution, and crystallizing), is stated to assume two different forms; regular hexagonal needle-shaped prisms and thick rhombic columns of $71\frac{3}{4}^0$; it is very soluble in water and in spirit of wine, and is not altered by the air. The strontia-salt (prepared like the baryta-salt) deliquesces slowly in moist air. The lime-salt (which is best prepared by decomposing the silver-salt with lime-water) crystallizes in prisms, deliquescent in the air, and insoluble in absolute alcohol. The ammonia-salt (prepared by decomposing the silver-salt with chloride of ammonium) forms needle-shaped crystals, stable in the atmosphere and readily decomposed by a gentle heat (*vide infra*). The magnesia-salt (prepared by boiling the silver-salt with magnesia) forms a leafy deliquescent mass, insoluble in absolute alcohol and readily decomposed by heat. Nitrite of silver (prepared by decomposing nitrate of silver with one of the above salts) forms a white hair-like powder or yellow fibrous crystals, prisms of 59^0, soluble at the ordinary temperature in 300 parts of water, and readily dissolving at the boiling heat (*vide infra*). Double salts with potassa are produced by mixing solutions of metallic nitrites with nitrite of potassa (the latter being in excess). Nitrite of protoxide of silver and potassa crystallizes in plates and prisms; it is somewhat yellow and permanent in the air, decom-

(1) J. Pr. Chem. XLI, 227.
(2) Pogg. Ann. LXXIV, 115; Ann. Ch. Pharm. LXVIII, 224 (in abstr.); J. Pr. Chem. XLVI, 318.

posing when slightly heated. Nitrite of protoxide of palladium and potassa forms yellow (in one experiment red) crystals. Nitrite of lead and potassa forms orange-yellow, six-sided monoclinometric crystals. Nitrite of protoxide of nickel and potassa forms brownish-red octohedrons; nitrite of protoxide of cobalt and potassa a yellowish powder. Nitrites.

Nitrite of Ammonia.—Millon(1) has observed, that an aqueous solution of nitrite of ammonia is decomposed by ebullition into water and nitrogen gas, especially if a drop of hydrochloric, sulphuric, or nitric acid be added; on the other hand, addition of ammonia prevents the decomposition. He obtains nitrite of ammonia by passing the vapour disengaged in the distillation of nitrate of lead through a solution of ammonia placed in a freezing mixture; the solution being evaporated over caustic lime in an atmosphere containing ammonia, this salt crystallizes first.

Nitrite of Protoxide of Lead.—Nicklès(2) has investigated the neutral nitrite of protoxide of lead, which presents the same crystalline form as the nitrate, (regular octohedron), and crystallizes with it. He found in the first 5·82 to 5·87 percent of water; PbO, NO_3 + HO requires 5·47. He compares the formula of both salts thus:



$$N \left.\begin{matrix} O_4 \\ H \end{matrix}\right\}, PbO \; ; \; N \left.\begin{matrix} O_4 \\ O \end{matrix}\right\}, PbO.$$

Nitrite of Protoxide of Silver.—According to Persoz(3) nitrate of protoxide of silver evolves oxygen even below redness, being partially converted into the nitrite. The latter is stated to be readily decomposed at a higher temperature, unless nitrate be still present; the decomposition may likewise be prevented by the addition of nitrate of potassa or soda. For the preparation of nitrite of silver, he recommends to heat equal parts of nitrate of silver and nitrate of potassa; from the hot aqueous solution the nitrite of silver will be deposited in crystals. This salt AgO, NO_3 forms fine needles, very slightly soluble in cold water.

Nitric Acid.—Kuhlmann(4) has adduced several new arguments for the production of nitric acid from ammonia by the action of

(1) Ann. Ch. Phys. [3] XIX, 255; Ann. Ch. Pharm. LXIV, 232; J. Pr. Chem. XL, 369.
(2) Compt. Rend. XXVII, 244; J. Pr. Chem. XLV, 374.
(3) Ann. Ch. Phys. [3] XXIII, 48; Ann. Ch. Pharm. LXV, 177; J. Pr. Chem. XLV, 98.
(4) Ann. Ch. Phys. [3] XX, 223; J. Pr. Chem. XLI, 289; Ann. Ch. Pharm. LXIV, 233.

Nitric acid. nascent oxygen. Nitric acid is liberated by the action of sulphate of ammonia and sulphuric acid upon bichromate of potassa, binoxide of manganese, binoxide of lead or minium, or binoxide of barium. By heating sulphate of ammonia with either chlorate or nitrate of potassa, the ammonia is completely converted into nitrous acid.

Mohr(1), Wackenroder(2), and Wittstein(3) have interchanged their views and experience regarding the best method of preparing nitric acid free from hydrochloric, whether by precipitation with silver, or by fractional distillation.

A. Smith(4) has communicated an investigation on the hydrates of nitric acid. By passing hot dry air through strong fuming acid he obtained a liquid of spec. grav. 1·503, which contained 81·56 percent NO_5. It commenced to boil at 88°, the temperature rising during the distillation to 121°, when a liquid remained in the retort containing 63·11 percent NO_5. The distillate between 88° and 93°, of a strong red colour, contained 84·96 percent; this portion when decolorized by a current of hot air exhibited a spec. grav. 1·516 at 15°·5. Its boiling point was found to be 84°·4, nearly all distilling between this temperature and 86°·7; it contained 84·54 percent NO_5. The first portion of the distillate which came over in the preparation of this acid had, after decolorization, similar properties (spec. grav. 1·517 at 15°·5, boiling point 84°·4) and contained 84·74 percent of NO_5 (NO_5+HO requiring 85·7); when diluted with water so as to produce an acid of the formula NO_5+2HO it had a spec. grav. at 15°·5 of 1·486, but no constant boiling point. The acid NO_5+4HO prepared by farther dilution had a spec. grav. of 1·424 at 15°·5, and distilled unchanged at 121°, the boiling point rising towards the end of the operation to 127°. Dilute acid, when heated until the boiling point was stationary at 121°, exhibited a spec. grav. of 1·412.

Action of Hydrosulphuric Acid upon Nitric Acid.—Leconte(5) has described the action of hydrosulphuric acid upon pure aqueous nitric acid of a spec. grav. of 1·33 (36°). His experiments contribute but little to what is already known upon this subject. The separated sulphur he found to be soft, similar to that which has been sud-

(1) Arch. Pharm. [2] XLIX, 25, L. 19.
(2) Arch. Pharm. [2] L, 23.
(3) Repert. Pharm. [3] I, 44.
(4) Chem. Soc. Mem. III, 399; Phil. Mag. [3] XXXI, 454.
(5) Ann. Ch. Phys. [3] XXI, 180; Ann. Ch. Pharm. LXIV, 233; J. Pr. Chem. XLII, 379.

denly cooled after fusion; the evolved gas consisted of binoxide of nitrogen and hyponitric acid, which, after some time, was replaced by undecomposed hydrosulphuric acid. He confirms the formation of sulphate of ammonia. Hyponitric acid produces with hydrosulphuric acid, sulphur, water and binoxide of nitrogen; hydrosulphuric acid and binoxide of nitrogen do not act upon each other in the dry state. Action of hydrosulphuric acid upon nitric acid.

Sulpho-nitric Acid.—Schönbein(1) has investigated the deportment of sulpho-nitric acid (a mixture of sulphuric and hydrated nitric acids) with sulphur, selenium, phosphorus and iodine. Sulphur or selenium are converted into sulphurous or selenious acid even in the cold; phosphorus into phosphoric acid and a small quantity of phosphorous acid; the addition of water to the acid after its action upon sulphur, selenium or phosphorus, causes a copious evolution of binoxide of nitrogen; the same is observed also after its action upon iodine. Nitro-sulphuric acid dissolves the latter body without at first changing colour; but after a short time, a sulphur-yellow powder separates from it, which Schönbein believes to consist of iodic acid with an oxide of iodine and sulphuric acid.

The action of a mixture of fuming nitric and sulphuric acids upon a number of organic compounds has been studied by Cahours(2); the results we shall communicate below, (*vide* anisic acid, benzoic acid, cuminic acid, mesitilole and salicylate of oxide of methyl).

Nitro-hydrochloric Acid (Aqua Regia).—Gay-Lussac(3) has published an investigation on aqua regia. Most chemists were of opinion that nitric and hydrochloric acids gave rise to the liberation of chlorine and nitrous or hyponitric acid, but in a separate state. E. Davy, however, stated, as early as 1831, that chloride of sodium, acted on by nitric acid, evolved together with chlorine a peculiar gas consisting of equal volumes of binoxide of nitrogen and chlorine; and Baudrimont in 1843 condensed, from the gaseous products of the action of nitric acid upon hydrochloric acid, a dark, reddish-brown liquid, of a spec. grav. 1·368, boiling at —7°, having a density of vapour = 2·49 and the

(1) Chem. Gaz. 1847, 229; Pogg. Ann. LXX, 87.

(2) Ann. Ch. Phys. [3] XXV, 5 (complete); J. Pr. Chem. XLVI, 321; Compt. Rend. XXIV, 553 (partly and in abstr.); Ann. Ch. Pharm. LXIV, 396; LXIX, 230; J. Pr. Chem. XLIII, 298.

(3) Ann. Ch. Phys. [3] XXIII, 203; Ann. Ch. Pharm. LXVI, 213; J. pr. Chem. XLIV, 335; Compt. Rend. XXVI, 619 (in abstr.); Instit. 1848, 181; J. Pharm. [3] XIV, 92; Gerhardt's Critical Remarks in Laurent's and Gerhardt's Compt. Rend. des Trav. Chim. 1849, 37.

Nitro-hydrochloric acid (aqua regia). composition $NO_3\ Cl_2$, to which he assigned the name chloro-nitric acid.—Gay-Lussac observed that aqua regia, when heated in a water-bath, evolves a gaseous body, which, dried and exposed to a frigorific mixture, separates into chlorine and a dark lemon-yellow liquid, boiling at -7^0. This liquid contains the elements of binoxide of nitrogen and chlorine, the latter is entirely converted, by the action of water, into hydrochloric acid. Gay-Lussac found this yellow liquid to contain 69·4 and 69·5 percent of chlorine, the calculated quantity for the formula NO_2Cl_2 being 70·2. In the gaseous state, this compound consists of equal volumes of binoxide of nitrogen and chlorine, it may be considered as hyponitric acid, in which two equivalents of oxygen are replaced by two equivalents of chlorine; hence, Gay-Lussac termed it *acide hypochloronitrique*, hypochloronitric acid.

Aqua regia, however, prepared under a variety of conditions, gives by no means always a condensable liquid of the adduced composition. In conjunction with it, and in variable quantity, a compound is formed which may likewise be obtained by mixing chlorine and binoxide of nitrogen. Both gases combine with diminution of volume, the mixture assuming an orange-yellow colour and condensing between -15^0 and -20^0 to a dark reddish-brown liquid, which, however, contains according to Gay-Lussac, more chlorine than the pure compound. The composition of the latter was ascertained by Gay-Lussac, by determining the diminution of volume exhibited by chlorine and binoxide of nitrogen, when mixed in various proportions; he arrived at the conclusion that one volume of chlorine combines with two volumes of binoxide of nitrogen, giving rise to a compound $NO_2\ Cl$. With reference to the composition of nitrous acid, he calls it *acide chloronitreux*, chloronitrous acid.

Now, the fluid which may be condensed from the vapour of aqua regia consists of a mixture, in variable proportions, of $NO_2\ Cl_2$ and the more volatile body $NO_2\ Cl$; the difference in volatility, however, is too small to admit of perfect separation. The former fluid, when treated with water, gives rise to hydrochloric acid and the products of hyponitric acid with water; if NO_2Cl predominates, water disengages binoxide of nitrogen. The vapour of this fluid is absorbed by concentrated sulphuric acid, which assumes a greenish-yellow colour, chlorine and hydrochloric acid being evolved.

Both of the above-named compounds, together with chlorine and water, are produced in the mutual reaction of the constituents of aqua regia, especially on application of heat. Gay-Lussac refutes the assertion of E. Davy and Baudrimont, that the properties of

Nitro-hydrochloric acid (aqua regia).

aqua regia are due to its containing a compound of chlorine, nitrogen and oxygen, and confirms the generally received view, that its action depends upon the presence of free chlorine. From the vapour evolved in the action of aqua regia upon gold, a liquid may be condensed, which is nearly of the composition NO_2Cl_2, containing, however, no free chlorine.

With aqua regia-silver, mercury and copper evolve binoxide of nitrogen; arsenious acid, phosphorus and protochloride of iron act in a similar manner. Tin and the metals which decompose water dissolve in aqua regia, particularly if it contains a large proportion of hydrochloric acid, without evolution of gas, in consequence of the formation of ammonia. Protochloride of tin evolves protoxide of nitrogen.

Finally, Gay-Lussac proves that a mixture of hydrochloric and hyponitric acids also dissolves gold; Sir H. Davy(1) had asserted that gold remains intact in a mixture of hydrochloric and concentrated nitric acids, saturated with binoxide of nitrogen.

Atmospheric Air.—Regnault(2) has determined the weight of a litre of dry atmospheric air at 0^0 and under a pressure of 760^{mm} for Paris, at 1·293187 grm. Biot and Arago had previously found for it 1·299541 grm. According to this determination of Regnault's, and his experiments upon the densities of other gases weighed under the usual normal conditions, one litre of

Nitrogen	weighs	1·256167	grm.
Oxygen	„	1·429802	„
Hydrogen	„	0·089578	„
Carbonic acid	„	1·977414	„

Doyère(3) announced that from the 1st of September to the 20th of December, 1847, the volume of oxygen in the air of Paris fluctuated between 20·5 and 21·5 vol. percent. Regnault, by a number of determinations made from the 24th to the 31st of December 1847(4), found it to vary between 20·90 and 21·00, in January, 1848(5), between 20·89 and 20·99; the results obtained in the analysis of air at various hours of the same day were found to oscillate between the same limits. Doyère(6) still maintained that fluctuations between 20·5 and 21·2 occurred; the insufficiency

(1) Ann. Phys. [2] I, 327.
(2) Relation, &c. (see p. 52), 151; Pogg. Ann. LXXIV, 202.
(3) Compt. Rend. XXV, 928.
(4) Ibid. XXVI, 11, 156; Ann. Ch. Pharm. LXVIII, 221.
(5) Ibid. 155; J. Pr. Chem. XLIV, 49.
(6) Compt. Rend. XXVI, 193.

Atmospheric air.

of the arguments adduced has been again pointed out by Regnault(1).

R. F. Marchand(2) found the quantity of oxygen in the air in ten experiments to vary from 20·90 to 21·03, the mean being 20·97 vol. percent; the quantity of carbonic acid, as the mean of 150 experiments, he found in the proportion of 3·1 to 10000 volumes of air.

Respecting the presence of ammonia in the atmosphere, compare page 299.

R. A. Smith(3) states that he has found in water, through which expired air had been passed, sulphuric acid, chlorine and an organic substance similar to impure albumen; he states that the deterioration of air in places where many persons are confined, depends on the presence of this organic compound. He discusses, moreover, the contamination of the atmosphere by putrefactive processes.

Ammonia.—Kuhlmann(4) has pointed out several instances in which nitric acid is converted into ammonia; this conversion occurs in the following reactions, viz., of dilute sulphuric acid and zinc upon nitrate of potassa, (instead of employing sulphuric acid and zinc, hydrochloric acid and iron may be used); of dilute sulphuric acid (or hydrochloric acid) and sulphide of iron (or tersulphide of antimony) upon a nitrate, when sulphur is deposited; of hydrochloric acid and zinc upon the nitrate of a metallic oxide, the metal of which is precipitated by zinc (f. i. copper); of a solution of tersulphide of arsenic in caustic potassa upon nitre at a gentle heat (slowly); of sulphuric acid upon a solution of nitre in sulphide of potassium, the former acid being added gradually in excess, likewise slowly; of a weak solution of nitrate of potassa upon hydrated protoxide of iron and of tin, when gently warmed; of hydrosulphuric acid upon a solution of terchloride of antimony, in presence of nitrate of potassa.

Reichenbach(5), in reply to the question whether the nitrogen of the atmosphere contributes to the formation of ammonia, calls to mind the fact that neither wood-charcoal alone nor carbonate of potassa, maintained for a long time at a red heat, give rise to the formation of ammonia, while it is formed if both be mixed and heated with access of atmospheric air; he is of opinion that the production of ammonia in

(1) Compt. Rend. XXVI, 233.
(2) J. Pr. Chem. XLIV, 24.
(3) Phil. Mag. [3] XXX, 478; Instit. 1848, 379.
(4) Ann. Ch. Phys. [3] XX, 223; J. Pr. Chem. XLI, 289; Ann. Ch. Pharm. LXIV, 233.
(5) From: Berichte über die Mittheilungen von Freunden der Naturwissenschaften in W·n, I. 158, J. Pr. Chem. XLI, 56.

this case depends upon the previous formation of cyanide of potassium and cyanate of potassa, which are decomposed under the influence of vapour of water. Ammonia.

Kemp(1) has published some experiments upon the quantity of ammonia contained in the atmosphere; he passed air through chloride of mercury, which absorbed the ammonia; 24840 cubic inches (English) gave 1·8 milligrammes of ammonia.

Bicarbonate of Ammonia.—Bicarbonate of ammonia has been found in considerable quantity in a bed of guano on the western coast of Patagonia. This salt, which now occurs in commerce, has been examined by Ulex(2). It forms crystalline masses, presenting two directions of cleavage inclined at an angle of 112°; its specific gravity is 1·45; it has the composition $NH_4O, 2\,CO_2 + HO$.

Sulphate of Ammonia.—The formula of crystallized sulphate of ammonia NH_4O, SO_3 has been confirmed by Kühn(3); according to theory it contains 60·6 percent of sulphuric acid, experiment gave 59·7

Double Salts of Chloride of Ammonium.—Hautz(4) has investigated several double salts of chloride of ammonium with metallic chlorides of the magnesium series. The magnesium double salt is obtained of constant composition only by adding an excess of ammonia to a dilute solution of magnesia in hydrochloric acid; the liquid deposits large, colourless prisms of the rhombohedral system. The nickel double salt is obtained by mixing two parts of hydrochloric acid saturated with protoxide of nickel, with one part of hydrochloric acid saturated with ammonia, and exposing to slow evaporation. It affects the same form as the preceding salt. A cobalt-salt prepared in the same manner forms ruby-red crystals belonging to the monoclinometric system. These three double salts are of corresponding composition, namely, $NH_4Cl, 2\,Me\,Cl + 12\,HO$, in which Me = Mg, Ni or Co. The magnesium-salt loses 4 HO at 100°, the rest of its water at 135°.

In the same manner the double salts with chlorides of manganese, zinc, and copper were obtained. They crystallize in the monoclinometric system. The manganese-salt is of a pale-red colour, and dissolves in 1½ parts of water at the ordinary temperature; the zinc-salt is colourless and almost deliquescent; the copper-salt is bluish-green and soluble in two parts of water. Their composition is represented by the formula $NH_4Cl, 2\,Me\,Cl + 4\,HO$,

(1) Chem. Gaz. 1848, 99.
(2) Ann. Ch. Pharm. LXVI, 11.
(3) Arch. Pharm. [2] L, 281.
(4) Ann. Ch. Pharm. LXVI, 280.

Double salts of chloride of ammonium.

in which Me=Mn, Zn or Cu; the manganese-salt loses at 100^0 3HO. From all these salts the total amount of water is expelled at 135^0.

The zinc double salt NH_4Cl, Zn Cl+HO, previously prepared, has been obtained and analyzed again by Hautz.

Nitrate of Ammonia.—Townsend Harris(1) has examined nitrate of ammonia, which had been crystallized at the ordinary temperature or obtained by evaporation of a concentrated solution at 100^0. The salt had in both cases the same composition, NH_4O, NO_5. The crystalline form, however, appeared to be different. 100 parts by weight of water dissolve according to his experiments 185 of nitrate of ammonia at 10^0.

Metals in general. Alloys.—Crookewitt(2) has examined the proportions in which metals can combine chemically among themselves. By amalgamation and straining through chamois leather, he obtained crystalline metallic compounds, which approached nearest to the formulæ Au Hg_4 (spec. grav. 15·412), Bi Hg (10·45), Pb Hg (11·93), Cd_2 Hg_5 (12·615). With potassium he obtained two amalgams, K Hg_{20} and K Hg_{25}, with silver (by bringing mercury in contact with a solution of nitrate of silver), according to the quantity of mercury employed, Ag_5 Hg_{16}, $AgHg_2$, Ag Hg_3, Ag Hg_4; with zinc an amalgam, containing 29·4 percent of zinc. He prepared likewise other alloys and determined their specific gravities.

Cu_2 Sn_5 7·652	Cu_3 Zn_5 7·939		Sn Zn_2 7·096	Sn Pb_2 9·966
Cu Sn 8·072	Cu_3 Zn_2 8·224	Cu Pb 10·375	Sn Zn 7·115	Sn Pb 9·394
Cu_2 Sn 8·512	Cu_2 Zn 8·392		Sn_3 Zn 7·235	Sn_3 Pb 9·025

Hydrides of Metals.—Poggendorff(3) has shown that the black precipitate, produced under certain circumstances, in a solution of silver at the negative pole of a voltaic battery, is not a combination of silver with hydrogen, but merely silver in an exceedingly fine state of division. The precipitate obtained from solutions of bismuth, antimony or tellurium is likewise only finely divided metal: it is only from a slightly acid solution of sulphate of protoxide of copper, subjected to a current of moderate strength, that a blackish-brown hydride of copper is deposited at the negative pole, disengaging hydrogen after the current is interrupted.

(1) Compt. Rend. XXIV, 816; J. Pr. Chem. XLI, 345.

(2) Specimen chemicum de conjunctionibus chemicis metallorum; Amstelodami 1848 (also under the title: "Verhandeing over scheikundige metaal-verbindingen") J. Pr. Chem. XLV, 87 (in abstr.); Ann. Ch. Pharm. LXVIII, 289.

(3) Pogg. Ann. LXXV, 337; J. Pr. Chem. XLV, 65; Berl. Acad. Ber., Juni 1848; Instit. 1848, 303.

Potassium. Sulphate of Potassa.—Pasteur(1) has confirmed the fact known previously, that the form of crystals of sulphate of potassa is mostly compound, and that this becomes manifest by their optical comportment. Potassium. Sulphate of potassa.

Sodium. Chloride of Sodium.—According to R. Wagner(2) alcohol of 75° percent by weight, dissolves at 14° 0·661, at 15°·25 0·700, at 38° 0·736, at 71°·5 1·033 percent of chloride of sodium; alcohol of 95·5 percent dissolves at 15° 0·174, at 77°·25 0·171.

Lithium.—Rammelsberg(3) has found by many varied experiments, that sulphate of lithia gives no double salt (lithia-alum) with sulphate of alumina, neither does it form any with sulphates of magnesia or the protoxides of zinc, copper, nickel, cobalt, manganese, or iron.

Barium.—Berzelius had found for the atomic weight of barium, 68·39, Pelouze, at a later period, 68·64. Marignac(4) has, like Pelouze, endeavoured to determine it, by ascertaining how much silver is precipitated from a solution by a known weight of chloride of barium; he obtained the number 68·54.

Calcium. Lime.—Wittstein(5) has found that one part by weight of lime is soluble in 729 to 733 of water at the common temperature, and in 1310 to 1569 of boiling water; likewise that the deposit formed on exposure of lime-water to the air is really CaO, CO_2.

Sulphate of Lime.—Millon(6) has stated that sulphate of lime obtained by precipitation, as likewise ignited and moistened gypsum ($CaO, SO_3+2 HO$), loses three-fourths of its water at 80° to 85°, (about 15 percent.), whilst with the native gypsum and that artificially crystallized (from hydrochloric acid), this takes place only at 105° to 110°; the compound $2(CaO, SO_3)+HO$ being formed. The remaining fourth of the water is expelled from gypsum only at 200° to 300°. Plessy(7), on the other hand, stated that native as well as artificially crystallized gypsum, when heated in a current of hydrogen to 110°—115°, give off their whole amount of water; that gypsum heated in the open air to 110°—115°, loses 15 percent, about three-fourths of its water; and

(1) Compt. Rend. XXVI, 304; J. Pharm. [3] XIV, 380.
(2) J. Pr. Chem. XL, 448.
(3) Berl. Acad. Ber., Nov. 1848, 385.
(4) Arch. Ph. Nat. VIII, 269; Ann. Ch. Pharm. LXVIII, 212.
(5) Repert. Pharm. [3] I, 182.
(6) Ann. Ch. Phys. [3] XIX, 222; J. Pr. Chem. XL, 363; Phil. Mag. [3] XXX, 299.
(7) Compt. Rend. XXIV, 658.

Sulphate of lime.

that then a kind of pause ensues in the diminution of the water; that at 130° to 140°, however, 2 percent more of water are disengaged; that at 200° to 250° the gypsum becomes anhydrous, and that anhydrous gypsum also takes up again its whole amount of water of crystallization. Plessy doubted whether a definite compound 2 (CaO,SO_3) + HO was formed, as stated by Millon; the latter, on the contrary(1), did not believe that Plessy's experiments established a contradiction of his views; upon which Plessy(2) has shown more accurately, that according to his experiments crystallized gypsum loses water at as low a temperature as 95°—100°, and that at 110° 17—19 percent are expelled, being therefore more than should escape in the formation of the compound 2 (CaO, SO_3) + HO, assumed by Millon.

Magnesium.—Scheerer(3), by determining the amount of sulphate of baryta obtained by the decomposition of a weighed quantity of pure sulphate of magnesia, had found the equivalent of magnesium, as an average of six experiments, to be = 20·08. On being reminded by Berzelius, that the sulphate of baryta might still have contained sulphate of magnesia, he repeated the experiment, and found Berzelius' conjecture confirmed. Having made the necessary correction in his former experiments for this source of error, he now(4) estimates the equivalent of magnesium at 20·11.—Svanberg and Nordenfeldt(5) have determined how much magnesia is obtained from a known amount of oxalate of magnesia (MgO, C_2O_3 + 2 HO), and how much sulphate of magnesia from a known weight of magnesia; as the mean of several experiments they found the equivalent to be 20·35 by the first method and 20·37 by the second.

Magnesia.—The spec. grav. of anhydrous magnesia has been determined by H. Rose(6); he found the spec. grav. of a specimen, which had been subjected to the heat of a porcelain-furnace, to be 3·65, closely agreeing with the number (3·75), found by Scacchi for periklase (MgO with a little FeO).

Sulphate of Magnesia and Soda.—Miller(7) states, that the crystalline form of sulphate of magnesia and soda is monoclinometric; the crystals examined by him did not admit of a more accurate determination.

(1) Compt. Rend. XXIV, 695.
(2) Ibid. 812.
(3) Pogg. Ann. LXIX, 535.
(4) Pogg. Ann. LXX, 407.
(5) J. Pr. Chem. XLV, 473.
(6) Ibid. LXXIV, 437; J. Pr. Chem. XLIV, 229; Berl. Acad. Ber., April, 1848; Instit. 1848, 369.
(7) Chem. Soc. Mem. III, 391; Phil. Mag. [3] XXXI, 540.

Nitrate of Magnesia.—For the preparation of the compound of nitrate of magnesia and alcohol, Einbrodt(1) dissolved the nitrate of magnesia, containing 6 equivalents of water, in nearly absolute alcohol, and obtained from this solution crystals, which, after the lapse of two years, had changed to a yellowish layer of a concentrated aqueous solution and tufts of acicular crystals. The latter contained an amount of magnesia corresponding to $MgO, NO_5 + 6\ HO$, they were, however, of a square prismatic form, and not deliquescent. Nitrate of magnesia

Cerium.—Marignac(2) determined the equivalent of cerium, by ascertaining the quantity of chloride of barium necessary for the exact decomposition of a known amount of sulphate of protoxide of cerium, and found the number 47·26. Beringer had found 46·16, Rammelsberg 45·8, Hermann 46·0.

Marignac makes some other statements with reference to cerium. For the preparation of the mixture of oxides of cerium, lanthanium and didymium, he recommends to triturate the powdered cerite with sulphuric acid to a thick paste, to expose the resulting dry powder in an earthen crucible for a lengthened period to a heat just below redness, and to introduce the cooled mass very gradually into cold water, in which the sulphates of the above oxides dissolve. In separating sesquioxide of cerium according to Mosander's method, by means of nitric acid, Marignac found it necessary that no sulphuric acid should be present. The oxide obtained by ignition of the nitrate has approximately the composition $3\ CeO, 2\ Ce_2O_3$; when heated with sulphuric acid it yields a yellow sulphate of proto-sesquioxide of cerium, soluble in water, in the presence of excess of sulphuric or of nitric acid, to a dark reddish-yellow fluid, from which it may be reprecipitated as a yellow powder by much water; dried at 100° it has the composition $3\ CeO, 2\ Ce_2O_3, 4\ SO_3, 7\ HO$; on account of its insolubility it is adapted for the preparation of pure combinations of cerium. Sulphate of protoxide of cerium crystallizes, by a gradual evaporation of its aqueous solution, in rhombic pyramids with edges of 114° 12′ and 111° 10′, to which a more acute pyramid with edges of 99° 48′ and 95° 48′ is often seen attached.

Beryllium. Berylla.—H. Rose(3) has determined the specific gravity of berylla; after being heated to redness over a spirit-lamp, it gave 3·09 to 3·08; subjected to the heat of a porcelain-furnace,

(1) Ann. Ch. Pharm. LXV, 115; J. Pr. Chem. XLVI, 165; Chem. Gaz. 1848, 85.
(2) Arch. Ph. Nat. VIII, 265; Ann. Ch. Pharm. LXVIII, 212.
(3) Pogg. Ann. LXXIV, 433; J. Pr. Chem. XLIV, 228; Berl. Acad. Ber. April, 1848; Instit. 1848, 368.

Beryllium. Berylla. it had the spec. grav. 3·02 to 3·03. H. Rose prefers Berzelius's opinion respecting the equivalent of berylla, according to which, berylla is expressed by Be_2O_3, to the view which assumes the composition BeO, because with the former assumption, the specific volume of berylla is found to be very nearly equal to that of alumina.

Aluminum. Alumina.—H. Rose(1) has likewise determined the spec. grav. of alumina. When ignited over a spirit-lamp, it was found to be 3·87 to 3·90; when exposed to the heat of a wind-furnace for six hours, 3·75 to 3·725; when heated in a porcelain-furnace, it was 3·999. This agrees with the spec. grav. of native crystallized alumina, which is 4·0, according to Schaffgotsch's later experiments, both in ruby and sapphire. Corundum gave rather lower numbers, 3·90 to 3·97.

R. Phillips(2) has observed that hydrate of alumina, kept moist after precipitation or preserved under water, becomes difficultly soluble in acids after a few days.

Of an investigation by Jacquelain on alum, only the conclusions of the author have as yet been published(3). Reserving further details until we are in possession of the complete research, we will only mention here, that he believes he has found alum to contain only 22 atoms of water. Jacquelain admits sulphate of alumina to contain only 16 atoms of water.

Gerhardt(4) defends the formula generally adopted for alum. Without regarding the earlier observations of Geiger, Graham, and Hertwig on the action of heat and sulphuric acid on this double salt, he states that alum, when crystallized, lost $\frac{5}{6}$ths of its water at 120°, without becoming insoluble in this liquid, which it did, however, when exposed to 200°; this insoluble (anhydrous) alum could be likewise prepared by the action of concentrated sulphuric acid with the aid of heat on crystallized alum; if permitted to remain in contact with water eight or ten days, it was reconverted into the soluble alum.

"On the non-existence of lithia-alum," see p. 255.

Silicium.—Pierre(5) has endeavoured to determine the equivalent

(1) Pogg. Ann. LXXIV, 430; J. pr. Chem. XLIV, 226; Berl. Acad. Ber., April, 1848; Instit. 1848, 368.

(2) Chem. Gaz. 1848, 349. (3) Compt. Rend. XXIV, 441.

(4) J. Pharm. [3] XII, 65.

(5) Compt. Rend. XXVI, 523; Phil. Mag. [3] XXXIII, 162; complete, Ann. Ch. Phys. [3] XXIV, 286; Laurent and Gerhardt's Compt. Rend. des Trav. Chim. 1849, 170 (in abstr.).

of silicium and the formulæ of its compounds; he expects to arrive at the decision of these questions by the study of substitution-products of double chlorides, and of ether- and amidogen-compounds. As yet only the first part of his investigation has been published. Pierre here gives some general statements respecting the action of hydrosulphuric acid on the terchloride of silicium ($Si\,Cl_3$); he remarks that the chlorine of this compound may be replaced partially or completely by sulphur; in addition to the compound $Si\,S\,Cl_2$ (see p. 306), which is easily isolated, $Si\,S_2\,Cl$ might probably exist; $Si\,S_3$ could be obtained in the state of purity (as a residue of the distillation of crude sulphobichloride of silicium, $Si\,SCl_2$) Pierre shows that the formulæ for these compounds appear in the most simple form if the expression $Si\,Cl_3$ be adopted for terchloride of silicium, (when that of silicic acid will become $Si\,O_3$), that, on the contrary, they become exceedingly complicated, if the formulæ $Si\,Cl$ and $Si\,O$, or $Si\,Cl_2$ and $Si\,O_2$, be adopted for chloride of silicium and silicic acid. Silicium.

According to H. Kopp(1), the greater probability of the formulæ $Si\,O_3$ for silica, $Si\,Cl_3$ and $Si\,Br_3$ for chloride and bromide of silicium, is supported also by the fact that the two last substances present that difference in their boiling points, which would occur between compounds containing three equivalents of bromine in the place of chlorine (comp. p. 71).

Silicic Acid.—Doveri(2) has published some observations on silica, in which but few new facts are mentioned. He states, that on the addition of an acid to a solution of an alkaline silicate, more silica remains dissolved if the acid be added at once, than if it be poured in gradually, and more on employing a dilute than a concentrated solution; that an alkaline bicarbonate and carbonic acid precipitate silicic acid from an alkaline silicate in the gelatinous state, and that the same precipitate is produced by sulphurous and other weak acids. This gelatinous precipitate seems to dissolve on addition of water; this is, however, only apparently the case, as it merely becomes transparent, and may be separated from the water by filtration. Precisely the same is observed with the jelly of silicic acid, produced by the precipitation of terfluoride of silicium with water, on treatment with hydrochloric acid. Silicic acid separated in the presence of water and dried at the common temperature, whether

(1) Ann. Ch. Pharm. LXVII, 356; J. Pharm. [3] XV, 226; Laurent and Gerhardt's Compt. Rend. des Trav. Chim. 1849, 173.

(2) Ann. Ch. Phys. [3] XXI, 40; J. Pr. Chem. XLII, 194; Compt. Rend. XXV, 109 (in abstr.); Phil. Mag. [3] XXXI, 315; Ann. Ch. Pharm. LXIV, 256.

Silicic acid. obtained from an alkaline silicate by an acid, or from terfluoride of silicium by water, was found invariably to contain the same quantity of water, corresponding to the formula HO, Si O_3; at 100° a certain quantity of water is lost, the hydrate HO, 2 Si O_3 being formed. Finely powdered silicic acid decomposes alkaline carbonates, on being boiled with their solutions, and likewise bicarbonates by continued ebullition. Doveri decomposed protochloride of copper with silicate of potassa; the washed precipitate was treated with hydrochloric acid and the filtrate subjected to a current of hydrosulphuric acid, when, on filtering once more, a clear solution of silicic acid was obtained, which he freed from hydrosulphuric acid by ebullition. This solution gave, with alkalies, a precipitate of gelatinous silicic acid; when evaporated in vacuo over lime, stellated needles were deposited containing HO, Si O_3.

For the composition and classification of the silicates, the reader is referred to our Mineralogical Report.

Sulpho-bichloride of Silicium.—Pierre(1) states, that on passing the vapour of terchloride of silicium and hydrosulphuric acid, together with hydrochloric acid, through a red-hot porcelain tube, a liquid is produced which may be purified by rectification (the first portion of the distillate being terchloride of silicium with a little chloride of sulphur). This liquid fumes when in contact with the air, its odour calling to mind both that of chloride of silicium and hydrosulphuric acid; addition of water to it produces a disengagement of hydrosulphuric acid and a slight precipitate of sulphur; its spec. grav. is about 1·45 at 15°, its boiling point above 100°. It contains Si S Cl_2. The density of the vapour was found = 4·78 5·24, 5·23;—5·00 corresponds to a condensation into 3 volumes. (*V. supra*, p. 305).

Titanium.—The separation of a very large quantity of metallic titanium (at least 80 pounds) in an iron-furnace, at Rübeland in the Harz, has been described by Blumenau(2).

The equivalent of titanium, formerly determined by H. Rose at 24·3, and by Mosander at 23·7, has been the subject of experiments by Pierre(3). A weighed quantity of bichloride of titanium

(1) Compt. Rend. XXIV, 814; Ann. Ch. Pharm. LXIV, 259; J. Pr. Chem. XLI, 342; more complete Ann. Ch. Phys. [3] XXIV, 286; Ann. Ch. Pharm. LXIX, 73; J. Pr. Chem. XLVI, 65.

(2) Ann. Ch. Pharm. LXVII, 122.

(3) Ann. Ch. Phys. [3] XX, 257; J. Pr. Chem. XLII, 65; Ann. Ch. Pharm. LXIV, 2 0 (in abstr.).

was dissolved in water, and the amount of chlorine determined according to Gay-Lussac's method, (by measurement of the amount of a standard solution of silver, required for precipitation). He obtained varying results, the experiments, made with the first portions of a quantity of bichloride of titanium, always giving a rather larger amount of chlorine than did the last portions; he ascribes this to the decomposing action of the moist air (which had penetrated on opening the vessel). He considers 25·2 to be probably the most accurate result of his experiments. Titanium.

For the deportment of the acid titanates of the alkalies, we refer to our Report on Analytical Chemistry.

Sesquichloride of Titanium.—The experiments made by Ebelmen on titanium, the results of which were published in 1846(1), have since(2) been fully communicated.—On passing the vapour of bichloride of titanium ($Ti\,Cl_2$) with hydrogen through a red-hot tube, hydrochloric acid and a new compound ($Ti_2\,Cl_3$) are formed, the latter being deposited in the cooler part of the tube, in the form of brilliant broad scales of a dark-violet colour. It is very unstable; when heated to redness on platinum foil in the air, it disengages $Ti\,Cl_2$, leaving a residue of titanic acid; the same decomposition seems to take place slowly even at common temperatures. It is volatile, but less so than $Ti\,Cl_2$, when exposed to the air it does not fume, but deliquesces. It dissolves in water, heat being disengaged; the violet-red solution becomes gradually colourless on exposure to the air, titanic acid being deposited: on evaporation, the solution evolves hydrochloric acid, a blue oxychloride remaining. The aqueous solution affords, with alkalies, a dark-brown precipitate, changing rapidly, with disengagement of hydrogen, successively to black, blue, and finally to white. The alkaline carbonates produce nearly the same reaction; carbonic acid being at first liberated, and then hydrogen. Hydrosulphuric acid produces no effect; hydrosulphate of sulphide of ammonium affords a brown precipitate, which appears to be identical with that obtained by means of the alkalies, and changing likewise into white titanic acid.

$Ti_2\,Cl_3$ is an energetic reducing agent, separating sulphur from sulphurous acid, gold, silver and mercury from their salts, and suboxide of copper from salts of the protoxide; it decolourizes

(1) Instit. 1846, 225.
(2) Ann. Ch. Phys. [3] XX, 385; Ann. Ch. Pharm. LXIV, 269; J. Pr. Chem. XLII, 70; J. Pharm. [3] XII, 437.

Sesqui-chloride of titanium. $Ti_2 Cl_3$.

solutions of the sesquioxide of iron, with formation of the protoxide. When added in a small quantity to water, it induces the solution of the violet sesquichloride of chromium.

The quantity of hydrogen evolved in decomposing, by an alkali, a known weight of $Ti_2 Cl_3$ dissolved in water, corresponds to the amount calculated upon the assumption that the precipitate decomposes water, to form titanic acid.

The formation of $Ti_2 Cl_3$ in the manner described, is generally accompanied by the elimination of metallic titanium, which is deposited in a thin layer, reflecting the yellow rays, and transmitting blue. Small leaves of a golden-yellow substance are likewise found here and there; Ebelmen considers them to be probably Ti Cl.

Sesquioxide of Titanium.—Titanic acid, when exposed to a strong red heat in a current of dry hydrogen, becomes black, changing to $Ti_2 O_3$. This oxide can be reconverted into titanic acid only by roasting it at a very high temperature; nitric and hydrochloric acids have no action upon it. Sulphuric acid dissolves it with a violet colour; the solution, when concentrated *in vacuo* over lime, yields only minute quantities of crystals and dries up to a nodular violet mass; by boiling, the violet aqueous solution is decolourized, with deposition of titanic acid; it exhibits the same reactions as $Ti_2 Cl_3$. In the analysis of the dried salt-mass, Ebelmen obtained more sulphuric acid than corresponds to the formula $Ti_2 O_3, 3 SO_3$; the details are not given.

Bisulphide of Titanium.—Ebelmen found that the action of bisulphide of carbon on titanic acid, heated to redness, did not afford a product of constant composition. He obtained a definite substance, however, on passing hydrosulphuric acid and the vapour of $Ti Cl_2$ through a tube at a faint red heat; the interior of the tube became coated with brilliant crystalline laminæ of the colour of brass, which were altered on exposure to air, with a perceptible evolution of hydrosulphuric acid; they are dissolved by neither hydrochloric nor dilute sulphuric, but almost entirely by nitro-hydrochloric acid. When heated, this substance inflames and is transformed into titanic acid. Its composition is $Ti S_2$. At the conclusion of the preparation of the bisulphide, the retort in which the bichloride of titanium had been heated, and into which hydrosulphuric acid had penetrated, was found to contain an olive-greenish substance, which assumed a metallic lustre by pressure and was likewise $Ti S_2$; the formation of this substance consequently commences at a temperature near the boiling point of $Ti Cl_2$.

Ilmenium.—Hermann(1) has endeavoured to establish by new proofs the existence of a peculiar metal, ilmenium, in the so-called yttroilmenite of Miask; and H. Rose(2) has given his reasons for believing this mineral to be identical with the samarskite investigated by him, and the supposed ilmenic acid to be, not a peculiar substance, but niobic acid, containing more or less impurities. Ilmenium.

Tantalum. Tantalic Acid.—The spec. grav. of tantalic acid has been examined by H. Rose(3). The acid obtained from the chloride, heated over a spirit-lamp until it exhibited the phenomenon of incandescence, had a spec. grav. of 7·03 to 7·53; by strong and lengthened ignition, the spec. grav. rose to 7·99 and even to 8·26. In general, a greater density and a more distinct crystalline state were found to be parallel; yet remarkable anomalies were exhibited, as f. i. a decrease in the spec. grav. of an acid which, once ignited, was again exposed to a higher temperature. The above experiments were made with an acid prepared from the tantalite of Finland; the acid from yttrotantalite of Ytterby had the spec. grav. 7·43.

Niobium. Niobic Acid.—H. Rose(4) has likewise determined the spec. grav. of niobic acid. This substance, prepared from the columbite of Bodenmais, when heated until exhibiting the phenomenon of incandescence, had the spec. grav. 4·96 to 5·12; when ignited for some hours in a wind-furnace 4·56, and when exposed to the heat of a porcelain-furnace for a lengthened period 4·60; acid of another preparation had under the first circumstances the spec. grav. 5·25 to 4·76, after the second treatment 4·58, after the third 4·59. Acid prepared from the North American columbite showed, under the first conditions, the spec. grav. 5·26 to 4·66; under the third, the constant number 4·60. The acid prepared from the samarskite (uranotantalite) of Miask had, in the first case, the spec. grav. 5·26 to 4·69, in the third 4·63 to 4·69. With a lower spec. grav., it had a more distinctly crystalline texture. Rose concludes that the acid can be obtained both in the amorphous and crystalline states, and that it is denser in the former; the amorphous acid is stated to be produced by the rapid decomposition of the chloride with water, and the crystalline, by gradual action of humid air on the chloride, and by the heat of the porcelain-furnace.

(1) J. Pr. Chem. XL, 457; Ibid. XLII, 129.
(2) Pogg. Ann. LXXI, 157; LXXIII, 449.
(3) Ibid. LXXIV, 285; Berl. Acad. Ber. März, 1848 (in abstr.); J. Pr. Chem. XLIV, 223; Ann. Ch. Pharm. LXVIII, 166; Instit. 1848, 367.
(4) Pogg. Ann. LXXIII, 313; Ann. Ch. Pharm. LXVIII, 165 (in abstr.)

Pelopium. Pelopic acid.

Pelopium. Pelopic Acid.—H. Rose(1), finally, has made experiments to determine the spec. grav. of pelopic acid. Prepared from the columbite of Bodenmais, by decomposing the chloride, and heated over a spirit-lamp until it exhibited the phenomenon of incandescence, it had the spec. grav. 5·98; exposed to a red heat for some hours in a wind-furnace 6·37; and ignited in a porcelain-furnace (when it had become crystalline) 5·79. Acid of a different preparation showed, in the first case, 5·95, in the second 6·09. After exposure to the heat of a porcelain-furnace, this acid was soluble only with difficulty in fused sulphate of potassa. The acid thus obtained, had, in the first case, the spec. grav. 6·14, in the second 6·48, in the third 5·83. Another preparation of acid from the chloride gave, in the first case, the number 5·70, in the second 6·32, in the third 5·79. A fifth specimen obtained by decomposing the chloride, immediately after preparation, with water, gave the spec. grav. 6·24 in the first instance, 6·42 in the second, and when heated for a greater length of time 6·73. Acid formed slowly by exposure of the chloride to the air, had, on ignition over a spirit-lamp, the spec. grav. 6.24; a crystallized specimen prepared from the acichloride 5·49.—Lastly, an acid prepared from the North American columbite (by gradual decomposition of the chloride of pelopium in the air) had the spec. grav. 6·10, and on ignition in a porcelain-furnace 6·17.—Rose distinguishes three different modifications of pelopic acid. The amorphous modification of the highest spec. grav., and obtained by heating freshly prepared chloride of pelopium with water; a crystalline modification, of a less spec. grav., formed by slow decomposition of the chloride exposed to the air; and a second crystalline modification of a constant spec. grav., and produced by ignition of the acid in a porcelain-furnace.

Tungsten.—Percy(2) has endeavoured in vain to obtain an alloy, applicable to technical purposes, of tungsten with any other metal.

Tungstates.—Laurent(3) concludes, from his researches on the tungstates, that there are at least five or six different tungstic acids. He states that these acids form different salts with ammonia which, when heated, yield tungstic acid, possessing different

(1) Pogg. Ann. LXXIV, 85; Ann. Ch. Pharm. LXVIII, 165 (in abstr.); J. Pr. Chem. XLIV, 220; Arch. Ph. Nat. VIII, 215.
(2) Chem. Gaz. 1848, 349.
(3) Ann. Ch. Phys. [3] XXI, 54; J. Pr. Chem. XLII, 116; Compt. Rend. XXV, 538 (in abstr.) the homotungstates, RO, $W_5 O_{15}$, are also mentioned here as a sixth class of salts; J. Pharm. [3] XIII, 53.

properties, according to the ammonia-salt employed. Laurent distinguishes the following species of salts, their composition being expressed in the more generally adopted notation. Tungstates.

1. *Tungstates:* RO, WO_3, with or without water (R representing a metal or hydrogen). With these are classed the potassa-, soda-, and baryta-salt, and the majority of the insoluble tungstates. Acid salts of this species are not known. The solution of a tungstate, when added to an excess of dilute nitric acid, produces a gelatinous precipitate. The hydrate of this tungstic is formed by the action of nitro-hydrochloric acid on tungsten.

2. *Paratungstates:* 2 RO, W_4O_{12}, with or without water. To this class belong the salts hitherto described as bitungstates of potassa, soda, ammonia, baryta, or strontia. They are slightly soluble in water, with the exception of the soda-salt; when in contact with warm water, they are immediately dissolved on addition of a very little dilute nitric acid, a portion of the paratungstic acid being precipitated.

3. *Metatungstates:* RO, W_3O_9, with or without water. The ammonia-salt of this class is formed when a solution of paratungstate of ammonia is boiled for some hours; the solution, when filtered after cooling and evaporated to a syrupy consistency, yields octohedrons which are very soluble. The solution, of this salt is not precipitated by concentrated hydrochloric acid.

4. *Isotungstates:* RO, W_2 O_6, with or without water. The ammonia-salt is prepared by boiling metatungstate of ammonia with excess of ammonia. It is slightly soluble in water. The acid, which may be separated by the addition of another acid, is characterized principally by reproducing the isotungstate with ammonia.

5. *Polytungstates:* perhaps 3 RO, W_6O_{18}. If the yellow acid obtained from the tungsten (wolfram) of mineralogists, be treated with ammonia, the solution, when slowly evaporated, at first deposits paratungstate, and then isotungstate of ammonia; the mother-liquor separates into two layers, of which one is brown and syrupy, and dries into an easily soluble crystalline mass, probably a double salt of ammonia and iron. It yields with boiling concentrated hydrochloric acid a white precipitate of polytungstic acid, which is not gelatinous, and does not become yellow by boiling; polytungstic acid is characterized by forming a very soluble salt with ammonia, which becomes gummy on evaporation.

Laurent has communicated formulæ for a large number of individual salts belonging to these different classes, without giving, however, any data by which a judgment could be formed res-

Tungstates. pecting the admissibility of his formulæ. Many are constructed according to his and Gerhardt's view, that fractions of an equivalent may exist in combinations, *i. e.* that one equivalent of a proximate constituent may be represented by varying quantities of different (and not even isomorphous) metals, and of hydrogen; *e.g.* by $\frac{3}{24}$K. $\frac{3}{24}$Na, $\frac{14}{24}NH_4$, $\frac{4}{24}$H; a view which we cannot allow to have been established. The communication of the formulæ, adduced for the individual salts may consequently be delayed until the publication of the analytical details.

Tungstate of Ammonia.—Kerndt(1)has examined the crystalline form of tungstate of ammonia, $NH_4O, 2WO_3 + HO$. In a treatise on the crystalline form, and the composition of the compounds of tungsten, of which only the examination of the mineral tungsten (wolfram) has as yet appeared(2), he propounds the opinion, that tungstic acid contains 2 equivalents of oxygen to 1 equivalent of metal, without, however, assigning any reasons.

Molybdenum.—Svanberg and Struve(3) have published extensive researches on the equivalent of molybdenum, and on the compounds of this metal. They found the former to be = 45·96, by determining the quantity of carbonic acid expelled on fusing a weighed quantity of molybdic acid with an excess of alkaline carbonate; the number 46·06 was obtained by ascertaining how much molybdic acid is formed when a known weight of sulphide of molybdenum is roasted.

Molybdates.—After stating the manner in which they prepared pure molybdic acid, the authors proceed to describe a number of its salts.—*Molybdate of potassa* $2(KO, MoO_3) + HO$ (when dried over sulphuric acid), is obtained by treating an ammonia-salt with an excess of carbonate of potassa, evaporating at a gentle heat to a syrupy consistency, and exposing the mass to a low temperature; the same compound separates as an oily mass on agitation of an alcoholic solution of caustic potassa with trimolybdate of potassa. It crystallizes in four-sided prisms, which are easily soluble in water, deliquesce slowly, and attract carbonic acid on exposure to the air; on heating, this salt falls to powder, water being evolved; it fuses by the strongest heat of a spirit-lamp and solidifies on cooling into a crystalline mass, which crumbles when perfectly cold to a white

(1) J. Pr. Chem. XLI, 190. (2) Ibid. XLII, 81.

(3) From the Memoirs of the Stockholm Academy for 1848, in J. Pr. Chem. XLIV, 257; Phil. Mag. [3] XXXIII, 409, 524; in part, Instit. 1849, 21; Ann. Ch. Pharm. LXVIII, 209, 293.

powder.—*Bimolybdate of potassa* could not be obtained. A double salt, with trimolybdate of potassa, $3 (KO, 2 MoO_3) + (KO, 3 MoO_3) + 6 HO$ or $3 (KO, MoO_3) + 5 (KO, 3 MoO_3) + 12 HO$, crystallizes from a solution of molybdic acid in carbonate of potassa, when concentrated nitric or hydrochloric acid is added carefully until the precipitate at first produced ceases to be perfectly dissolved; the salt is decomposed by water into the difficultly soluble trimolybdate and molybdate of potassa.—*Trimolybdate of potassa*, $KO, 3 MoC_3 + 3 HO$, is most easily obtained in the manner just described; when gradually separated, it appears in the form of needles, with a beautiful silky lustre; when rapidly deposited, it is obtained as a voluminous white precipitate. This salt is nearly insoluble in cold, but very soluble in boiling water, from which it separates only very slowly on cooling. On ignition, it loses its water of crystallization, and becomes very difficultly soluble even in boiling water; it is converted, when ignited in hydrogen, into the neutral salt, with formation of $2 MoO_2$ or MoO, MoO_3.—By the addition of nitric acid in excess, to a solution of molybdic acid in carbonate of potassa, sometimes the *quadrimolybdate*, sometimes the *quinquimolybdate of potassa* is precipitated as a white powder; both are anhydrous, insoluble in water, easily fusible, and solidify on cooling with crystalline texture. The existence of several other potassa-salts was traced; they were not, however, more minutely examined. Molybdates.

Molybdate of soda, prepared by fusing together MoO_3 and NaO, CO_2 in the proper proportions, is a white crystalline mass, easily and completely soluble in water, from which it crystallizes, as $NaO, MoO_3 + 2 HO$, in small rhombohedrons, which easily fuse with elimination of water.—*Bimolybdate*, prepared by the same method as the preceding salt, is obtained as a white crystalline mass, which, stirred with water, separates into acicular crystals, difficultly soluble in cold, and slowly in hot water; from the solution $NaO, 2 MoO_3 + HO$ crystallizes with difficulty.—*Trimolybdate of soda* separates after some time as a voluminous precipitate on the careful addition of concentrated nitric acid to a strong solution of molybdic acid in carbonate of soda; it is more soluble than the corresponding potassa-salt, and crystallizes as $NaO, 3 MoO_3 + 7 HO$.—When heated in hydrogen, it exhibits the same deportment as the corresponding potassa-salt.—An excess of nitric acid added to a solution of molybdate of soda separates nothing in the cold; on ebullition, however, molybdic acid is immediately separated.

Molybdate of ammonia is obtained by treatment of an excess

Molybdates. of molybdic acid with a concentrated solution of ammonia in a closed bottle, precipitation by alcohol and dessication over caustic lime; it forms microscopic four-sided prisms of the composition NH_4O, MoO_3; water converts it into an acid salt.—*Bimolybdate of ammonia* separates as a white crystalline powder, $NH_4O, 2\ MoO_3$, when a solution of molybdic acid in ammonia, (the latter being present in excess), is rapidly evaporated.—From a solution of molybdic acid in ammonia, a combination of bimolybdate and trimolybdate of ammonia $NH_4O, 2\ MoO_3 + NH_4O, 3\ MoO_3 + 3\ HO$ crystallizes out in six-sided prisms. Other salts were formed by the action of nitric acid on a solution of molybdic acid in ammonia; they were not, however, investigated any further by the authors.

The *baryta-salts* are obtained by the decomposition of the potassa- or soda-salts with chloride of barium; it is, however, difficult to free them completely from an admixture of the alkaline salts. Molybdate of baryta, BaO, MoO_3 is precipitated as a fine crystalline powder, on the addition of a solution of chloride of barium to a solution of molybdic acid in excess of ammonia; it is difficultly soluble in water, and infusible.—Svanberg and Struve doubt the existence of the basic baryta-salt described by Heine(1).—$BaO, 3\ MoO_3 + 3\ HO$ is formed by the decomposition of the corresponding potassa-salt, as a white flocculent precipitate, somewhat soluble in water, and becoming horny after dessication; it fuses and solidifies on cooling with crystalline structure; $BaO, 2\ MoO_3 + BaO, 3\ MoO_3 + 6\ HO$ prepared by the decomposition of the corresponding ammonia-salt, is a flocculent, amorphous precipitate, tolerably soluble in water and fusible. By treatment of the molybdate of baryta with dilute nitric acid, the nonomolybdate $BaO, 9\ MoO_3 + 4\ HO$ is obtained; it crystallizes in small six-sided prisms, insoluble in water, and fusible.

A solution of trimolybdate of potassa gives with nitrate of protoxide of lead a white powder, *molybdate of protoxide of lead*, PbO, MoO_3, fusible only at a high temperature. The oxide appears to enter into combination with molybdic acid in one proportion only.

Molybdate of protoxide of silver, AgO, MoO_3, is obtained as a flocculent yellow precipitate, by the addition of nitrate of protoxide of silver to a solution of molybdate of potassa; it blackens on exposure to the air, and is slightly soluble in pure water, but easily so in water containing nitric acid. Trimolybdate of potassa gives,

(1) J. Pr. Chem. IX, 204.

with nitrate of protoxide of silver, a flocculent yellowish-white precipitate, perhaps $AgO, 3\ MoO_3 + AgO, 2\ MoO_3$. Molybdates.

Deportment of Molybdic Acid with Phosphoric Acid.—Svanberg and Struve have made voluminous communications on the phenomena exhibited by molybdic acid, when under the influence of phosphoric acid, without however bringing this subject so far towards a conclusion, as to allow of a brief and yet complete abstract being given. Molybdic acid, when coloured yellow by the action of phosphoric acid, dissolves easily in ammonia; on addition of acids to this solution, an amorphous lemon-yellow precipitate is produced, which is insoluble in water and acids; the same compound may be obtained by dissolving molybdic acid in an excess of ammonia, mixing with phosphate of soda, applying heat and adding sulphuric, hydrochloric or nitric acid. The yellow precipitate is, according to Svanberg and Struve, quinquimolybdate of ammonia, $NH_4O, 5\ MoO_3 + HO$, containing, however, some phosphoric acid. If the ammonia be expelled by warming with potassa, a colourless solution is produced, in which acids produce a crystalline yellow precipitate of quinquimolybdate of potassa, $KO, 5\ MoO_3 + 2\ HO$. The solution of the yellow ammonia-salt in an ammonical liquid gives, with chloride of barium, a white molybdate of baryta, the precipitate becoming yellow, however, on the addition of acid. It has not been accurately ascertained on what depend the altered reactions exhibited by molybdic acid in the presence of phosphoric acid.

Sesquioxide of Molybdenum.—According to Kobell(1) molybdic acid, when dissolved in an excess of acid, is deprived of half its oxygen by copper, a sesquioxide Mo_2O_3 remaining in solution instead, as was hitherto believed, of a binoxide of molybdenum MoO_2, the existence of which is doubted by Kobell.

Vanadium.—Vanadium has been discovered by Deck(2) in the iron slag of Staffordshire.

With regard to pervanadic acid, see perchromic acid.

Chromium.—Some new experiments have been made by Moberg(3) upon the atomic weight of chromium, which had been determined by Berzelius at 28·1, by Péligot at from 26·0 to 26·4, and by Berlin at 26·3. In determining the quantity of sesquioxide of chromium which remained after igniting the sulphate, he found the numbers 26·5 to 26·8, according as the salt employed had been heated to 330°, or to a dull redness. In an experiment

(1) J. Pr. Chem. XLI, 158. (2) Chem. Gaz. 1848, 298.
(3) J. Pr. Chem. XLIII, 114; J. Pharm. [3] XIV, 76.

Chromium.

conducted in a similar manner with sulphate of sesquioxide of chromium and ammonia, he found from 26·7 to 26·9.—According to Jacquelain's(1) statement the equivalent of chromium is only 25.

Protoxide and Protochloride of Chromium.—According to Moberg(2), protochloride of chromium, when dissolved in water, decomposed by potassa, and the precipitate washed and dried, (oxygen being perfectly excluded), yields a dark-brown hydrate of protoxide of chromium $CrO + HO$, which, when ignited in hydrogen, is converted into sesquioxide of chromium, the water of hydration being decomposed. He has confirmed the composition $Cr\,Cl$ of protochloride of chromium by a new analysis(3), and has examined the action of several salts upon a solution of this chloride(4); we will mention here only, that with acetate of soda, a red liquid is obtained, from which acetate of protoxide of chromium $CrO, C_4H_3O_3 + HO$ (as Péligot had already found) is deposited in oblique rhombic columns; with succinate of soda, a precipitate is formed which is scarlet when moist, becoming lighter and partially blueish-grey when dried *in vacuo;* its composition is $CrO, C_4H_2O_3 + HO$; with benzoate of potassa, a bright reddish-grey precipitate is obtained, which, when dried, has the composition $CrO, C_{14}H_5O_3$, and when exposed to the air changes colour in a similar manner. Moberg(5) has farther communicated his views respecting the possible existence of protoxide of chromium in nature, namely, in chrome-iron, and especially in pyrope.

Sesquioxide of Chromium.—According to Fremy(6) hydrate of sesquioxide of chromium, precipitated in the cold from one of its salts, and dried at the ordinary temperature in a current of air, has the formula $Cr_2\,O_3 + 9\,HO$ (experiment gave 51·6; theory requires 51·4 percent of water). Its green alkaline solution, when boiled, gives a precipitate of hydrated sesquioxide of chromium $Cr_2\,O_3 + 8\,HO$, which is soluble in alkalies (experiment 49·3, calculation 48·4 percent of water).

According to Lefort(7) the salts of sesquioxide of chromium produce with the carbonates, and bicarbonates of the alkalies, either a hydrate of peculiar composition, or a compound $Cr_2\,O_3, CO_2 + 4\,HO$;

(1) Compt. Rend. XXIV, 679; J. Pr. Chem. XLI, 348.
(2) J. Pr. Chem. XLIII, 125; Ann. Ch. Pharm. LXVIII, 303.
(3) Ibid. XLIV, 322; Ann. Ch. Pharm. LXVIII, 304.
(4) Ibid. 327; Ann. Ch. Pharm. LXVIII, 305.
(5) J. Pr. Chem. XLIII, 119.
(6) Ann. Ch. Phys. [3] XXIII, 388; J. Pr. Chem. XLV, 196.
(7) Compt. Rend. XXVII, 269; J. Pharm. [3] XV, 24, (entire).

the former is obtained by employing the green modification of sulphate of sesquioxide of chromium, the latter by using the blue. The carbonate loses 3 HO between 75° and 150°; the carbonic acid and last atom of water are not expelled below 300°. Sesquioxide of chromium.

Traube(1) contests, that sesquioxide of chromium, which has been heated to redness, is actually soluble in hot concentrated sulphuric acid. According to his experiments, the insoluble red sulphate of sesquioxide of chromium, which is obtained by heating a solution of hydrated sesquioxide of chromium in dilute sulphuric acid, and adding concentrated sulphuric acid, consists of 2 (Cr_2O_3, 3 SO_3) + HO, SO_3 (Schrötter had given the formula Cr_2O_3, 3 SO_3). The same salt is formed as the final product of the action of concentrated sulphuric acid at a high temperature upon bichromate of potassa, and chrome-alum; its formation in this case, however, is preceded by bodies containing sulphate of potassa. This salt, when heated in an atmosphere of hydrosulphuric acid, is converted into sesquisulphide of chromium; in hydrogen gas, into a mixture of Cr_2O_3 and Cr S in variable proportions. Experiments made to obtain corresponding compounds of sesquioxide of iron and alumina were unsuccessful.

For preparing the blue crystallized modification of the sulphate of sesquioxide of chromium, Traube(2) recommends the gradual addition of spirit of wine, drop by drop, to a solution of chromic acid in dilute sulphuric acid; or the exposure of the solution to the vapour of ether.

Sulphate of Sesquioxide of Chromium and Potassa.—Of an investigation of chrome-alum, by Jacquelain(3), the conclusions only have as yet been published, we therefore confine ourselves to mentioning that, according to his statements, chrome-alum contains only 22 atoms of water.

Chromate of Sesquioxide of Chromium.—According to Traube(4), dry chromic acid is not affected by sulphurous acid at 100°; at 180°, however, it is reduced to the state of chromate of sesquioxide of chromium.—Cr_2O_3, 3 CrO_3 is obtained as a black mass, by heating chromic acid; by treatment with water its composition is not altered; on ebullition, however, it is changed from the insoluble to the soluble modification. Aqueous chromic acid is converted by alcohol into a chromate of sesquioxide of chromium, 3 Cr_2O_3, 2 CrO_3.

(1) Ann. Ch. Pharm. LXVI, 87.
(2) Ibid. LXVI, 168.
(3) Compt. Rend. XXIV, 439.
(4) Ann. Ch. Pharm. LXVI, 103, 106, 108.

Sesqui-chloride of chromium.

Sesquichloride of Chromium.—According to the statements of Jacquelain(1), the unwashed violet chloride of chromium consists of a mixture of Cr_2Cl_3 and $CrCl$; he also gives some observations upon the solubility of the sesquichloride of chromium at various temperatures, both in open and closed vessels.—Moberg(2) obtained from the aqueous solution of sesquichloride of chromium the compound $Cr_2Cl_3 + 12 HO$, already investigated by Péligot; the crystals however, were not granular, but needle-shaped.

Chromic Acid.—For the preparation of chromic acid, Traube(3) recommends to heat gently 1 part of bichromate of potassa, with 3½ parts of sulphuric acid, and 2½ parts water, and to decant from the sulphate of potassa deposited on cooling, when on farther addition of 4 parts of sulphuric acid, chromic acid will commence to separate. The liquid is heated, and water added until the crystals are dissolved, the solution is now evaporated until a pellicle forms upon the surface, and allowed to crystallize. The acid, dried on a porous tile, may be purified by careful fusion in an air-bath, when the chromate of potassa and sulphuric acid produce an insoluble compound of sesquioxide of chromium; or, by dissolving in water, adding sulphuric acid until a precipitate begins to appear, evaporating and slowly crystallizing.

Chromates.—For the preparation of chromates, Jacquelain(4) recommends to start from the lime-salt; chrome-iron is heated with common chalk, the mass being frequently stirred; the finely divided product is suspended in hot water, acidulated with sulphuric acid, and freed from sesquioxide of iron by chalk: the solution contains bichromate of lime, and a minute quantity only of sulphate.

Darby(5) has found that bichromate of ammonia cannot be regarded as a compound of oxide of ammonium, its composition being $NH_3, 2 CrO_3$. For the neutral salt, he has confirmed the recognized formula NH_4O, CrO_3. By mixing solutions of equal equivalents of bichromate of ammonia and chloride of mercury, large, deep-red, readily soluble crystals are obtained, of the composition $NH_3, 2 CrO_3 + HgCl$. The double salt, already analysed by Millon, $KO, 2 CrO_3 + HgCl$ is obtained in a similar manner in the form of magnificent red spear-like crystals.

(1) Compt. Rend. XXIV, 679; J. Pr. Chem. XLI, 348; Ann. Ch. Pharm. LXIV, 275, (in abstr).
(2) J. Pr. Chem. XLIV, 325. (3) Ann. Ch. Pharm. LXVI, 165.
(4) Compt. Rend. XXIV, 504; Ann. Ch. Phys. [3] XXI, 478, (in detail); J. Pr. Chem. XLIII, 202.
(5) Chem. Soc. Qu. J. I, 20; Ann. Ch. Pharm. LXV, 204; J. Pharm. [3] XIII, 369.

Chromates.

Darby found, like Millon, the brick-red precipitate which is produced on addition of protochloride of mercury to neutral chromate of potassa to be $3HgO, CrO_3$; by evaporating the solution, filtered from this precipitate, small reddish crystals are obtained of the formula $KO, CrO_3 + 2\ HgCl$ readily dissolving in water to a yellow solution. This compound is likewise obtained by mixing both constituents in proper proportions, sufficient hydrochloric being added to dissolve the precipitate which is formed. The formula $2\ (KO, CrO_3) + 3\ HgCy$, assigned by Rammelsberg to the double salt, obtained from a solution of equal equivalents of these bodies, in bright-yellow large leafy crystals, has been confirmed by Darby. If a solution of this salt be completely precipitated by nitrate of silver, and heated nearly to ebullition with sufficient nitric acid to redissolve the precipitate, a splended needle-formed double salt is obtained on cooling, of the composition $AgO, 2CrO_3 + HgCy$.—Chromate of suboxide of mercury (Hg_2O, CrO_3), is obtained in the form of a crystalline bright brick-red powder, by boiling the precipitate $4Hg_2O$, $3\ CrO_3$, produced by chromate of potassa and nitrate of suboxide of mercury; a chromate of the suboxide is likewise obtained by mixing $2\ (KO, CrO_3) + 3\ HgCy$ with nitrate of protoxide of mercury, and boiling the resulting precipitate with a small quantity of nitric acid until dissolved, when on cooling Hg_2O, CrO_3 is precipitated as a beautiful brilliant-red crystalline powder.

Perchromic Acid.—Barreswill(1) has given a more minute description of his experiments, communicated(2). at an earlier period, upon the existence of perchromic acid, which is obtained by mixing chromic acid with dilute binoxide of hydrogen, (or bichromate of potassa with a dilute, but very acid solution of binoxide of barium in hydrochloric acid), when a liquid is formed of a blue colour, which is removed from the aqueous solution by ether. Both the aqueous and the etherial solutions are rapidly decomposed with evolution of oxygen, no chromic acid, but sesquioxide of chromium being formed. He obtained combinations with quinine and strychnine only; but even these compounds, which are of a dirty-violet colour, are rapidly decomposed. From the amount of oxygen disengaged by a weighed quantity of bichromate of potassa, after conversion into the blue compound, (which, by treatment with

(1) Ann. Ch. Phys. [3] XX, 364; J. Pr. Chem. XLI, 393; Ann. Ch. Pharm. LXIV, 275, (in abstr.)

(2) Inst. 1846, 320.

Perchromic acid. hydrochloric acid is changed into Cr_2Cl_3), Barreswil assigns the formula Cr_2O_7 to the oxide of chromium generated under the adduced circumstances.

Vanadiate of ammonia gives in the same manner a blood-red colour, which is somewhat more stable.

Uranium.—Péligot(1) has published a more detailed account of his experiments (communicated in 1846) (2), on the equivalent of uranium: he has found, on burning the oxalate of sesquioxide of uranium, and comparing the carbonic acid produced with the remaining green proto-sesquioxide, that the equivalent approached the more closely the number 60, the purer the salt that he employed; he believes to have confirmed this number, by some new analyses of the acetate of the sesquioxide. Berzelius(3) has pointed out some particularities in Péligot's statements which lead to results contradictory to the views of this chemist respecting the true equivalent of uranium.

Phosphate and Arseniate of Sesquioxide of Uranium.—Werther(4) has investigated the compounds of sesquioxide of uranium with phosphoric and arsenic acids; both acids combine with one, two, and, perhaps, also three equivalents of the base.—Sesquioxide of uranium, when treated with phosphoric acid, forms a bright yellow mass, which partially dissolves on boiling; the yellow solution, when evaporated over sulphuric acid, yields lemon-yellow crystals $U_2O_3, PO_5 + 5HO$, which, on gently heating, become of a dull, and, subsequently, of a bright yellow colour; the last equivalent of water is evolved only at a red heat. The crystallized salt is decomposed by water, phosphoric acid and a small quantity of sesquioxide of uranium being separated, and a polybasic salt remaining behind.—Sesquioxide of uranium, when treated with dilute phosphoric acid, and washed, forms an uncrystallizable bright-yellow powder $2U_2O_3, PO_5 + 4HO$, which is insoluble in water and acetic acid, but soluble in mineral acids and in excess of carbonate of ammonia; at a temperature between 120° and 170° it loses three equivalents of water, the fourth equivalent being driven off only at a much higher temperature. When exposed to a red heat it becomes of a dark yellow; but on cooling again assumes

(1) Ann. Ch. Phys. [3] XX, 329; J. Pr. Chem. XLI, 398.
(2) Compt. Rend. XXII, 487; J. Pr. Chem. XXXVIII, 152.
(3) Jahresbericht, XXVII, 89.
(4) Phil. Mag. [3] XXXIII, 244, 246; J. Pr. Chem. XLIII, 321; Berl. Acad. Ber. May, 1848, (in abstr.); Ann. Ch. Pharm. LXVIII, 312; Instit. 1848, 393; J. Pharm. [3] XIV, 57.

its bright appearance. Phosphoric acid, when added to acetate of sesquioxide uranium, produces a precipitate of somewhat darker colour than the preceding, exhibiting the same deportment even at a red heat; when dried in the air, its composition is represented by the formula $2\ U_2\ O_3,\ PO_5 + 9\ HO$, dried at 60^0 by $2\ U_2\ O_3,\ PO_5 + 7\ HO$; this formula likewise represents the precipitate produced by the treatment of nitrate of sesquioxide of uranium with $NaO,\ 2\ HO,\ PO_5$, or, with the fluid remaining after the incomplete decomposition of $3\ NaO,\ PO_5$ by nitrate of sesquioxide of uranium.—Nitrate of the sesquioxide of uranium produces with an excess of $3\ NaO,\ PO_5$ (too great an excess almost entirely dissolves the precipitate which is formed) a dark-yellow precipitate, insoluble in water and containing $5\ U_2O_3$ and $1\ NaO$ to $2\ PO_5$, which is probably a mixture; the same view is entertained by Werther respecting the residue left on treating the precipitate in question with so large a quantity of $3\ NaO,\ PO_5$ that the precipitate is partially redissolved. Phosphate and arseniate of uranium.

The salt $U_2O_3,\ AsO_5 + 5\ HO$ deposits in small yellow crystals, when pure nitrate or acetate of sesquioxide of uranium is boiled with excess of a solution of arsenic acid, and the fluid evaporated over sulphuric acid; like the preceding phosphate it is decomposed by water, it is soluble (as also are the following compounds) in mineral acids and in carbonate of ammonia, but not in acetic acid. At a temperature of 150^0, it loses three equivalents of water, and at a strong heat it decomposes into arsenious acid, oxygen, and a polybasic salt.—The yellow precipitate, obtained by the action of arsenic acid upon acetate of sesquioxide of uranium, or of water upon a mixture of arsenic acid and nitrate of sesquioxide of uranium, which has been boiled to drive off the excess of nitric acid, is, when dried over sulphuric acid, $2\ U_2O_3,\ AsO_5 + 9\ HO$, and loses at 120^0 eight equivalents of water. The precipitate produced by arseniate of potassa in the nitrate of the sesquioxide, probably also contains $2\ U_2O_3$ to $1\ AsO_5$, but a different amount of water, and a variable quantity of potassa. The pale-yellow precipitate produced on addition of $3\ NaO,\ AsO_5$ to nitrate of sesquioxide of uranium was found to contain $NaO,\ 2\ U_2\ O_3,\ AsO_5 + 5\ HO$. —According to a more recent communication of Werther(1) $2\ U_2\ O_3,\ AsO_5 + 9\ HO = 2U_2\ O_3,\ HO,\ AsO_5 + 8\ HO$, when boiled with basic acetate of protoxide of copper, yielded a greenish salt of the formula $2\ U_2\ O_3,\ CuO,\ AsO_5 + 8\ HO$.

(1) J. Pr. Chem. XLIV, 127.

Manganese. Carbonate of protoxide of manganese.

Manganese. Carbonate of Protoxide of Manganese.—The precipitate produced, both in cold and hot solutions of protoxide of manganese, by carbonates or bicarbonates of the alkalies, is, according to Lefort(1), $MnO, CO_2 + HO$. At about 90° it loses part of its water; the entire quantity may be expelled without in any degree impairing the white colour of the precipitate.

Salts of Sesquioxide of Manganese.—In addition to the phosphate of sesquioxide of manganese (see p. 214) Herrmann(2) has studied several other salts of the sesquioxide, but without obtaining any satisfactory results. Tartaric, oxalic, and malic acids produce by their action upon the sesquioxide, carbonic acid and salts of the protoxide.

Permanganic Acid.—Some reactions of permanganic acids have been described by Schönbein(3), with the view of more distinctly exhibiting the analogy between this body, binoxide of hydrogen and ozone; with regard to his experiments upon the formation of this acid, the reader is referred to pages 204 and 205.

Arsenic.—As to the researches which have proved a considerable distribution of arsenic upon the earth's surface, we refer to our Report of the analyses of mineral waters.

Schönbein(4) advances the opinion, that the production of the garlic odour from arsenic does not depend upon the formation of a suboxide, but rather of a peculiar modification of arsenious acid $As_2 O_6$, which is afterwards converted into ordinary arsenious acid $2 AsO_3$.

H. Becker(5) has performed experiments upon the precipitation of arsenic by means of hydrosulphuric acid. According to his observations, arsenic in solution, whether in the form of arsenious, or arsenic acid, is not entirely precipitated, either by hydrosulphuric acid, or by the alkaline sulphides; the quantity, however, of arsenic remaining dissolved is in most cases (except in legal inquiries) quite immaterial, if the liquid, saturated with hydrosulphuric acid, be allowed to stand some time at a gentle heat in well-closed vessels, (six or eight days). Becker recommends to saturate from time to time with hydrosulphuric acid, lest a small quantity of sulphide of arsenic be re-dissolved in the acid liquid, and to filter off the precipitate before expelling the hydrosulphuric acid.

Arsenious Acid.—Some farther statements have been communicated by Pasteur(6), upon the isodimorphism of arsenious acid and

(1) Compt. Rend. XXVII, 268; J. Pharm. [3] XV, 18 (complete).
(2) Pogg. Ann. LXXIV, 303.
(3) J. Pr. Chem. XLI, 228.
(4) Pogg. Ann. LXXV, 377.
(5) Arch. Pharm. [2] LVI, 287.
(6) Chem. Gaz. 1848, 308; J. Pharm. [3] XIV, 399.

teroxide of antimony, discovered by Wöhler. Potassa, when saturated with arsenious acid at the boiling temperature, gradually deposits this acid in right rhombic crystals, which is the form of native teroxide of antimony. Teroxide of antimony may be obtained in regular forms, by digesting freshly precipitated and washed algaroth-powder, for several days, with excess of carbonate of soda; under the microscope, it presents the appearance of octohedrons or cubo-octohedrons, which are not to be distinguished from the ordinary form of arsenious acid. Arsenious acid.

Bussy(1) has contributed some new observations to the numerous contradictory statements regarding the solubility of arsenious acid. The glacial is said to dissolve more rapidly and freely in water than the opaque variety; the same quantity of water which dissolved from 36 to 38 parts of the former, at 12^0 to 13^0, was not capable of taking up more than from 12 to 14 parts of the latter; in the strictest sense of the term, neither of the two modifications of this acid exhibited a peculiar solubility. (Of what value, then, are these statements respecting solubility?) The opaque variety of acid, when continuously boiled with water, was converted into the glacial; *i. e.*, it acquired the solubility of the latter, 110 grm. of acid dissolving in one litre of fluid. The continued influence of water and low temperature converted the glacial into the opaque variety, *i. e.*, the strength of the solution diminished until the quantity, remaining dissolved, corresponded to the opaque variety. That both modifications of acid may exist in solution, explained the anomaly which had been observed regarding the solubility of this substance. Fine division increased the solubility of the opaque, and diminished that of the glacial acid. The acid which had been rendered opaque by ammonia, and that which had been crystallized from water, exhibited the same deportment with water. The opaque variety dissolved more slowly in dilute hydrochloric acid than the glacial modification. Both kinds exhibited the same deportment with litmus.

Arsenites.—Pasteur(2) and Filhol(3) have published researches upon the salts of arsenious acid. According to Pasteur, solution of potassa, when mixed in the cold with excess of AsO_3, gives rise to a slight evolution of heat, an oily non-crystallizable fluid being pro-

(1) Phil. Mag. [3] XXXI, 151; Compt. Rend. XXIV, 774; Repert. Pharm. [2] XLVIII, 301; Ann. Ch. Pharm. LXIV, 286; J. Pr. Chem. XLI, 340; J. Pharm. [3] XII, 321 (most complete).

(2) Chem. Gaz. 1848, 309; J. Pharm. [3] XIII, 395; Ann. Ch. Pharm. LXVIII, 308.

(3) J. Pharm. [3] XIV, 331; Ann. Ch. Pharm. LXVIII, 308.

Arsenites. duced, which, when diluted and mixed with nitrate of silver, yields a yellow precipitate, the supernatant fluid presenting an acid reaction. This oily fluid, when mixed with alcohol, deposits, after one or two days, rectangular prisms of the composition $KO, 2AsO_3+2\,HO$; at 100^0 it loses 1 equivalent of water. This salt, when boiled for several hours with carbonate of potassa, yields a syrupy body KO, AsO_3, which is very slightly soluble in alcohol; mixed with excess of caustic potassa, the surplus being afterwards removed by alcohol, a salt of the composition $2\,KO, AsO_3$ is obtained, which is very soluble in water, and corresponds with the yellow silver-salt.—Filhol mentions a binarsenite of potassa, obtained in crystals, by exposing a concentrated solution for some time to a temperature of 40^0 or 50^0; respecting the water in this salt, no statements are made. He did not succeed in obtaining KO, AsO_3 in a state of purity, according to Pasteur's method.

Soda likewise forms three salts of a corresponding composition, the statements, however, of Pasteur and Filhol are very incomplete; the former did not succeed in crystallizing $2\,NaO, 2\,AsO_3$; the latter was unable to obtain NaO, AsO_3 in a state of purity.

According to Pasteur, arsenite of ammonia $NH_4\,O, AsO_3$, is immediately formed on addition of concentrated solution of ammonia to arsenious acid; a hard mass is obtained, apparently consisting of hexagonal tables, derived from an oblique rectangular prism. This salt remains permanent only, when in contact with liquid ammonia; alone, and in aqueous solution, it rapidly loses its ammonia; with nitrate of protoxide of silver, this solution gives a yellow precipitate of $2\,AgO, AsO_3$, the supernatant fluid presenting an acid reaction. An ammonia-salt, corresponding with the silver-compound, has not yet been obtained.

Filhol has not succeeded in obtaining definite compounds of arsenious acid with either lime or magnesia. With baryta, he formed two compounds; BaO, AsO_3 is obtained by mixing binarsenite of potassa or soda with excess of chloride of barium, when arsenious acid is liberated, and the compound separates, either immediately or gradually, as a white gelatinous magma, or as a dendritic, but amorphous mass; in this state it is easily soluble in water, while, when dried, it forms a white insoluble powder. Quite analogous in its properties is $2\,BaO, AsO_3$, which is prepared by decomposing $2\,KO, AsO_3$ with BaCl. In a similar manner PbO, AsO_3, and $2\,PbO, AsO_3$, may be obtained. In addition to the above-mentioned silver-compound $2\,AgO, AsO_3$, he has formed a salt of the composition $3\,AgO, AsO_3$; by the addition of a solution of arsenious acid to

excess of nitrate of protoxide of silver, saturated with ammonia, the latter salt is obtained of a beautiful yellow colour, which in the light rapidly changes to green, and at a temperature from 140° to 150° suddenly becomes black, only a trace of water being evolved; at a higher temperature this compound fuses with disengagement of arsenious acid. Arsenites.

Terchloride of Arsenic and Ammonia.—Pasteur(1) believes, that the product obtained by the action of ammoniacal gas upon terchloride of arsenic, (consisting, according to H. Rose, of $2\ As\ Cl_3 + 7\ NH_3$,) is $2\ (Cl\ As\ NH) + 4\ (Cl\ NH_4) + NH_3$; when heated, ammonia is first evolved, then sublimes the whole; chloride of ammonium, however, chiefly towards the end of the process. When boiled with water, this product decomposes into ammonia, arsenious acid, and chloride of ammonium; with cold water, a slight evolution of heat takes place, ammonia being disengaged, while the liquid deposits on evaporation a precipitate consisting of six-sided tables, in which Pasteur found 13·4 percent of chlorine, 58·1 arsenic, 5·3 nitrogen, and 2·3 hydrogen. This body, when treated with ammonia, forms an arsenite NH_4O, AsO_3.

Teriodide of Arsenic.—For the preparation of teriodide of arsenic, pure arsenietted hydrogen (prepared by hydrochloric acid and arsenide of zinc) is recommended by Meurer(2) to be passed into a freshly prepared solution of iodine in alcohol until it is decolorized, when on evaporation, crystals of teriodide of arsenic are deposited.

Sulpho-arsenic Acid.—Cloez(3) has observed that sulpho-arseniate of potassa, $As_3\ O_3\ S_2,\ KO + 2\ HO$, is formed by passing hydrosulphuric acid through arseniate of potassa.

Antimony.—According to some experiments of Bensch(4), the success of Liebig's method of preparing metallic antimony, free from arsenic, is dependent on the presence of iron. To free from arsenic a regulus not containing any iron, it is necessary to add 2 percent of sulphide of iron, and to treat it according to Liebig's prescription. Meyer(5) recommends to heat antimony with 1¼ part of crude nitre, and ½ part of carbonate of soda to a low redness, to wash the antimoniate of soda, and to fuse it with half its weight of bitartrate of potassa.

Teroxide of Antimony.—The following method of preparing teroxide of antimony, (for the purpose of obtaining tartar-emetic, &c.) is

(1) Chem. Gaz. 1848, 309; J. Pharm. [3] XIII, 395; Ann. Ch. Pharm. LXVIII, 307.
(2) Arch. Pharm. [2] LII, 1.
(3) Compt. Rend. XXIV, 388.
(4) Ann. Ch. Pharm. LXIII, 273.
(5) Ibid. LXVI, 238.

Teroxide of antimony.

recommended by Hornung(1); a mixture of fifteen parts of finely-divided tersulphide of antimony and 36 parts of concentrated sulphuric acid are heated until sulphuric acid alone is volatilized; the product is then washed and decomposed with carbonate of soda.

Compounds of Teroxide of Antimony.—Several compounds of teroxide of antimony have been investigated by Péligot(2).

Sulphates. Algaroth-powder (for which Péligot proposes the formula $SbO_2\,Cl$, *vide infra*) gave with hydrated sulphuric acid a needle-shape salt, $SbO_3,\ 4\,SO_3$; teroxide of antimony produced with fuming sulphuric acid small brilliant crystals, $SbO_3,\ 2\,SO_3$, both compounds had been dried upon a porous tile in perfectly dry air, or *in vacuo*. Peligot states that he could not obtain the salt $5\,SbO_3$, $3\,SO_3$, which, according to Berzelius, is the neutral one (?). When treated with hot water, the salt described gave a basic compound, $2\,SbO_3,\ SO_3$, the composition of two other specimens thus obtained was pretty accurately expressed by the formula $2\,SbO_3\ SO_3 + 2\,HO$. (The salts $SbO_3,\ SO_3$ and $SbO_3,\ 3\,SO_3$, investigated by Brandes, are not mentioned by Péligot.)

Nitrate of teroxide of antimony, $2\,SbO_3\ NO_5$ is obtained in crystals of the lustre of mother of pearl, by addition of water to teroxide of antimony dissolved in fuming nitric acid.

Oxichlorides. By treatment of terchloride of antimony with cold water, Péligot obtained a precipitate, which after some days became crystalline; well washed, it exhibited a composition agreeing with the formula proposed for algaroth-powder. For this compound, he assumes the simpler composition $SbO_2\,Cl$; this requires 19·6 of chlorine for 75·1 of antimony, and 8·9 of oxygen; this oxichloride, however, has not yet been proved to have this composition. By the treatment of terchloride of antimony with hot water, another oxichloride, $SbO_2\,Cl + SbO_3$, is obtained; this formula corresponds to $Sb\,Cl_3 + 5\,SbO_3$, the composition usually adopted for algaroth-powder.

Bitartrate of teroxide of antimony crystallizes, after some time, from a thick syrupy solution of teroxide of antimony in tartaric acid. The crystals, according to Provostaye's(3) description, belong to the rhombic system (macrod: brachyd: principal axis = 1 : 0·9308 : 0·429; $\infty P.\ \infty \breve{P}\tfrac{3}{2}.\ \infty \bar{P}\ \infty.\ 3\,\breve{P}\,\infty.\ \bar{P}\,\infty$); they are easily soluble in water, deliquescent in moist air, and have the composition $SbO_3,\ 2\,C_8\,H_2\,O_8 + 12\,HO$; they lose their water at 160^0. On addition of alcohol

(1) Arch. Pharm. [2] L. 47.

(2) Phil. Mag. [3] XXXI, 230; Ann. Ch. Phys. [3] XX. 283; Ann. Ch. Pharm. XIV, 280; J. Pr. Chem. XLI, 376; J. Pharm. [3] XII, 210.

(3) Ann. Ch. Phys. [3] XX, 302; J. Pr. Chem. XLI, 392.

to a concentrated solution of this salt, a precipitate is formed which, when dried at 160°, is SbO_3, $C_8\,H_2\,O_8$, HO.—**Péligot** assigns the formula SbO_3, KO, $2\,C_8H_2O_8$, 8HO to the tartrate of teroxide of antimony and potassa first investigated by **Knapp**. **Teroxide of antimony.**

Péligot prepared *oxalate of teroxide of antimony* by boiling the teroxide with a solution of oxalic acid; by treating algaroth-powder with oxalic acid; by adding hydrochloric acid to a hot solution of oxalate of teroxide of antimony and potassa, when oxalate of teroxide of antimony is thrown down as a crystalline powder; or by adding oxalic acid to a solution of the same double salt. By these several processes, he obtained the same product, namely, a crystalline salt, insoluble in water, and of the composition SbO_3, $2\,C_2O_3$, HO. Boiling water decomposes it into oxalic acid and teroxide of antimony —To oxalate of teroxide of antimony and potassa, obtained by the action of binoxalate of potassa upon teroxide of antimony, **Bussy** had assigned the composition SbO_3, 3 KO, $6\,C_2O_3$, 6 HO; the correct formula, however, according to **Péligot**, is SbO_3, 3 KO, $7\,C_2O_3$, 8 HO.

Péligot is of opinion that a view ought to be taken of the composition of these salts, similar to that which he proposed for the compounds of uranium. The oxides which contain 3 equivs. of oxygen readily combine with 3 equivs. of acid, forming soluble salts; while the compounds with 1 equiv. of acid are usually insoluble in water. With the oxides of both uranium and antimony a different deportment is observed. The compounds of these oxides, with 1 equiv. of acid, according to **Péligot**, correspond to the salts which are formed by bases containing 1 equiv. of oxygen, with one equiv. of acid. He expresses this analogy by assuming in these compounds, the existence of peculiar oxygenated radicals, antimonyl and uranyl; when sesquioxide of uranium and teroxide of antimony become protoxides of uranyl and antimonyl, their composition being represented by the formulæ $(U_2\,O_2)$ O and (SbO_2) O.

Antimonic and Metantimonic Acid.—**Fremy**(1) has resumed the investigation of antimonic acid, and has found that it exists in two modifications, which form two perfectly distinct classes of salts. He assigns the term antimonic acid to the modification particularly studied by **Berzelius**, which forms with potassa a neutral salt which is gummy, and an acid salt almost insoluble in water; this modification is produced by heating antimony and nitre. For the hydrate of antimonic acid, obtained by precipitating the neutral

(1) Ann. Ch. Phys. [3] XXIII, 404; J. Pr. Chem. XLV, 209; Ann. Ch. Pharm LXVIII, 279.

Antimonic and metantimonic acids.

antimoniate of potassa with nitric acid, and dried at the ordinary temperature in a current of dry air, he found the composition $SbO_5 + 5HO$. According to Fremy's experiment, the neutral antimoniate of potassa, dried *in vacuo*, is represented by the formula $KO, SbO_5 + 5 HO$; exposed for several hours to a temperature of 160^0, it has the composition $KO, SbO_5 + 3 HO$, when it becomes insoluble in cold water, and dissolves in boiling water only after some time, with reassumption of the 2 equivs. of water; by continuous treatment with water, even the ignited compound KO, SbO_5 is reconverted into the soluble salt $KO, SbO_5 + 5HO$. The white compound formed by heating one part by weight of antimony with four parts of nitre, consists chiefly of KO,SbO_5.—For antimoniate of ammonia, see below.

Fremy applies the term metantimonic acid to the substance formed by decomposing pentachloride of antimony with water, and which is produced likewise by heating antimoniate of potassa with excess of potassa. He considers this acid to be bibasic, giving rise to the formation of two series of salts, $2 MeO, SbO_5$ (neutral salts), and MeO, HO, SbO_5 (acid salts). The former exist only in presence of a large amount of alkali; by the action of solvents, they are converted into acid salts.

The acid metantimonates MeO, HO, SbO_5 have the same composition as the neutral antimonates, or differ from them only by containing one equiv. of water: they are, too, converted into the latter under trifling influences. Metantimonic acid likewise readily passes, even in water, into antimonic acid. The accurate distinction between both modifications is thus rendered rather difficult. Fremy believes to have found a distinctive character in the deportment of the two acids with ammonia, antimonic being insoluble therein; the former is likewise said to dissolve more rapidly in acids than the latter. Metantimonic acid is perfectly soluble in a large amount of cold water, from which it is precipitated by acids. This hydrate has the formula $4 HO, SbO_5$.

Antimonic acid, when heated with a large excess of potassa, produces a neutral metantimoniate $2 KO, SbO_5$, which is stable only in a considerable amount of potassa, being converted, by the influence of water, into acid metantimoniate of potassa, $KO, SbO_5 + 7 HO$. This salt contains acid and base in the same proportion as the neutral antimoniate of potassa; the latter, however, is gummy, does not affect the salts of soda, and produces with chloride of ammonium a white flocculent precipitate, while the former compound is crystalline, and gives a white precipitate with salts of soda, but none with chloride of ammonium. The acid metantimoniate of potassa when dissolved in water is rapidly transformed into the antimoniate; the latter, when

gently dried, loses two equivs. of water, and is converted into metantimoniate; by too much drying, however, the above mentioned insoluble antimoniate of potassa $KO, SbO_5+3\ HO$ is formed.—For the preparation of metantimoniate of potassa, Fremy recommends the following method as successfully employed by him of late. One part by weight of antimony and four parts of nitre are heated to redness in an earthenware crucible; the insoluble antimoniate of potassa which forms, is washed and then boiled with water for two or three hours, the liquid evaporated being continually replaced. In this manner a solution of antimoniate of potassa is obtained which, when mixed with solid hydrate of potassa and evaporated until a sample taken out solidifies with crystalline texture, deposits on cooling a copious quantity of metantimoniate, which is dried on plates of unglazed porcelain. Before using it as a reagent for soda, the excess of alkali is separated by washing. The salt has to be preserved in the dry state, being converted, when kept in solution, into antimoniate. Antimonic and metantimonic acids.

Fremy(1) prepares the metantimoniate of ammonia by the continued action of a concentrated solution of ammonia upon hydrated metantimonic acid; the latter dissolves slowly with formation of a salt containing one equiv. of metantimonic acid and two equivs. of ammonia, which corresponds to the potassa-salt $2\ KO, SbO_5$. This salt is difficult to isolate; the addition of a drop of alcohol to its aqueous solution throws down a crystalline acid metantimoniate $NH_4O, SbO_5, 6HO$. This compound precipitates the salts of soda; when gently heated it loses water and becomes insoluble. In this state when boiled with water, it loses its crystalline appearance and is converted, without evolution of ammonia, into white insoluble antimoniate of ammonia. The latter is invariably produced if either antimonic or metantimonic acids be dissolved in boiling solution of ammonia, when it separates from the solution on cooling. Metantimoniate of ammonia can be obtained only in the cold, and even then it is often converted into the antimoniate, particularly, as it appears in the presence of an excess of ammonia. The acid metantimoniate of ammonia, though preserved in the dry and crystalline state in well-closed vessels, passes, even at the ordinary temperature, after a day or two into antimoniate, when it becomes insoluble in water.—The insoluble antimoniate of ammonia, when dried *in vacuo*, has the composition $NH_4O, SbO_5, 4\ HO$.

Pentasulphide of Antimony and Sulphide of Sodium.—This compound (Schlippe's salt), when crystallized, contains, according to

(1) Pogg. Ann. LXXIV, 376.

Bismuth. H. Rose, 18 equivs. of water, which agrees with Rammelsberg's determination. The compound, when fused with exclusion of air, crumbles, when afterwards exposed to the atmosphere, to a bulky powder, presenting under the microscope a crystalline appearance; 15 equivs. of water are absorbed in this change.

Bismuth.—The colours exhibited by bismuth, purified according to Quesneville's method, when exposed in either the dry or moist state to the atmosphere, have been obtained more rapidly, and quite at will, by Poggendorff(1) by means of galvanism. A bismuth-plate, when forming in a solution of 1 part of potassa in 4 to 6 parts of water, the positive electrode, in opposition to a platinum-plate as the negative electrode of a battery of two Grove's cells, successively assumes a yellow, red, violet, blue, and green colour, and becomes again colourless, in order to repeat the same series of changes, when the colours appear with less intensity. By interrupting the current at the proper time, a definite colour may be fixed.

Carbonate of Teroxide of Bismuth.—According to Lefort(2), the precipitate produced by alkaline carbonates in either cold or boiling solutions of bismuth, when nearly neutral, is represented by the formula BiO_3, CO_2, assigned to it by Heintz. Bicarbonates give rise to the formation of a compound BiO_3, $CO_2 + HO$, which loses its water at 100^0 to 120^0.

Nitrate of Teroxide of Bismuth.—Gladstone(3) has found that crystallized nitrate of teroxide of bismuth is represented by the formula BiO_3, $3\ NO_5 + 10\ HO$, a composition, which has been confirmed by Heintz's(4) experiments. It was formerly believed to contain 9 equivalents of water only. When exposed for several hours to a temperature of 150^0, it is converted into BiO_3, $NO_5 + HO$; at 260^0, both water and acid are evolved.

The decomposition of nitrate of teroxide of bismuth by water has been minutely examined by H. Becker(5). He finds that this compound, when acted on either in the dry state, or in the most acid solution, is first converted into a salt BiO_3, $NO_5 + 2\ HO$, which separates as a curdy precipitate, gradually changing into soft scales of the lustre of mother of pearl. These crystals, which under the microscope appear as elongated tables, readily lose a portion of their

(1) Pogg. Ann. LXXIV, 586; Berl. Acad. Ber. July, 1848; Instit. 1849, 13.

(2) Compt. Rend. XXVII, 268; J. Pharm. [3] XV, 25, (more in detail).

(3) Chem. Soc. Mem. III, 480; J. Pr. Chem. XLIV; 179; Arch. Pharm. [2] LVII, 40.

(4) J. Pr. Chem. XLV, 102.

(5) Arch. Pharm. [2] LV, 31, 129; Ann. Ch. Pharm. LXVIII, 282, (in abstr.)

water; dried at 100^0 they contain only half the amount expressed in the above formula. Freshly precipitated, this substance dissolves pretty easily in water, especially on addition of a few drops of nitric acid; this solubility ceases in the presence of a certain quantity of the common nitrate. The solution of this compound is very unstable, being decomposed, more or less rapidly according to the temperature and the amount of free acid present, into common nitrate, free nitric acid and basic products.—When acid and cold, the solution soon deposits brilliant prisms, $5\ BiO_3,\ 4\ NO_5 + 9\ HO$, the true *magisterium bismuthi*; the same compound is often formed on washing the precipitate produced on the addition of cold water to bismuth-solutions. To prepare the *magisterium*, according to this method, the precipitate is allowed to subside, and after separation of the acid liquid, left in contact with water, until the transformation has taken place. *Magisterium bismuthi* is not perceptibly soluble in cold water, which decomposes it but slowly; hot water extracts from it the neutral salt and free acid, a residue being left, which, especially after continued ebullition, is a dingy white and heavy powder, amorphous, when examined under the microscope, and in which from 1 to 2 per-cent of nitric acid were found.—A concentrated solution of bismuth, when evaporated at high temperatures, sometimes deposits white crystalline crusts, exhibiting under the microscope thick six-sided tables, and containing $5\ BiO_3,\ 4\ NO_5 + 12\ HO$; they are not altered by cold water acidulated with nitric acid, which on ebullition converts them into needles and prisms, most likely of *magisterium*; by the action of pure water the same deportment is observed as with the compound $BiO_3,\ NO_5 + 2\ HO$.—By treating the latter substance, or the crystallized neutral salt, or any acid bismuth-solution with boiling water, or by heating to ebullition an acid liquid with a precipitate formed by cold water, short prisms of the compound $6\ BiO_3,\ 5\ NO_5 + 9\ HO$ are formed. They are insoluble in water, which decomposes them gradually, but more rapidly than *magisterium bismuthi*; when washed upon a filter, until the washings cease to be acid, the residue is found to be converted into larger prisms of the composition $4\ BiO_3,\ 3\ NO_5 + 9\ HO$.—If the compound $BiO_3,\ NO_5,\ 2\ HO$ be treated with a large quantity of pure water, a nearly transparent solution is obtained, rapidly turning milky, and slowly depositing a very soft white powder of the formula $5\ BiO_3,\ 3\ NO_5 + 8\ HO$.—Becker extensively discusses the best method of preparing *magisterium bismuthi* for the purposes of practice.

Nitrate of teroxide of bismuth.

Diesel(1) has directed attention to the changes of colour, which

(1) Arch. Pharm. [2] LIII, 296.

Zinc. are exhibited by nitrate of teroxide of bismuth, when decomposed by heat.

Zinc.—Nicklès(1) states that zinc, prepared according to Jacquelain's method (by distillation in hydrogen gas) presented very distinctly the form of pentagonal dodecahedrons; hexagonal forms having been previously observed by Nöggerath, he considers zinc to be dimorphous.

Protoxide of Zinc.—Brooks(2) found the spec. grav. of pure crystallized protoxide of zinc to be 5·61 to 5·66.—W. and T. Herapath(3) have examined a specimen of crystallized protoxide of zinc, which had been deposited in an earthenware retort, used in the distillation of zinc. It formed a spear-like aggregate of small, brilliant, transparent, apparently square-prismatic crystals of 5·53 spec. grav., from which 88·5 to 92 percent of protoxide of zinc were removed by acids (without effervescence), a crystalline residue remaining behind, of the composition SnO_2, ZnO.

Hydrated Protoxide of Zinc.—Nicklès(4) found that hydrated protoxide of zinc, whose formula HO, ZnO he corroborates, affects right-rhombic forms: $\infty P \,.\, \infty \check{P} \infty \,.\, \infty \bar{P} \infty \,.\, \bar{P} \infty$; the angle of ∞P in the macrodiagonal principal section was found to be 62° 20′, that of $\bar{P} \infty$ in the same section 120° 41′; spec. grav. 2·677.

Salts of Protoxide of Zinc.—The precipitates produced by hydrosulphuric acid in solutions of zinc, dilute and insufficiently acidulated, have been examined by Riegel(5).

Carbonate of Protoxide of Zinc.—A boiling zinc-solution, when mixed with a solution of carbonate of potassa or soda, yields, according to Lefort(6), a precipitate of $8\,ZnO, 3\,CO_2 + 6\,HO$; he does not state at what temperature the compound was dried. The precipitate produced by bicarbonate of potassa or soda, in cold solutions of zinc, contains $3\,ZnO, CO_2 + 6HO$.

Sulphate of Protoxide of Zinc and Potassa. — According to Miller's(7) determination the crystals of sulphate of protoxide of zinc and potassa are monoclinometric: $\infty P \,.\, 0P \,.\, \infty P2 \,.\, +P \infty \,.\, -P$, combined with a clinodiagonal doma; orthodiagonal: clinodiagonal: principal axis $= 0{\cdot}744 : 1 : 0{\cdot}529$; the angle formed by the two

(1) Ann. Ch. Phys. [3] XXII, 37; J. Pharm. [3] XIII, 18; Pogg. Ann. LXXIV, 442.
(2) Pogg. Ann. LXXIV, 439.
(3) Chem. Soc. Qu. J. I, 42.
(4) Ann. Ch. Phys. [3] XXII, 31; J. Pharm. [3] XII, 406.
(5) Arch. Pharm. [2] LVI, 154.
(6) J. Pharm. [3] XI, 329; J. Pr. Chem. XLI, 126.
(7) Chem. Soc. Mem. III, 391; Phil. Mag. [3] XXXI, 540.

latter = 79°38′; ∞ P : ∞ P in the orthodiagonal principal section = 105°48′, ∞ P2 : ∞ P2 = 66°56′, + P ∞ : 0P = 150°6′.

Sulphate of protoxide of zinc and potassa.

Selenite of Protoxide of Zinc.—According to Wöhler's(1) experiments, a concentrated solution of selenious acid, when acted on by metallic zinc, yields selenide of zinc, free selenium and quadriselenite of protoxide of zinc $ZnO, 4\,SeO_2 + 3\,HO$, which very slowly crystallizes from the filtrate, when concentrated to a certain extent at a gentle heat, and exposed to spontaneous evaporation, as the concentrated solution is decomposed by heat. It forms large, yellow oblique rhomboidal columns which are permanent in the air, and easily soluble in water, forming an acid solution, which, on application of heat, is decomposed into selenious acid and neutral selenite of protoxide of zinc, which separates.

Nitrate of Protoxide of Zinc.—Gerhardt(2) states that he has obtained a basic salt of the composition $4\,ZnO, NO_5 + 3\,HO$, which was crystallized in prismatic needles.

Cadmium. Hydrated Protoxide of Cadmium has been obtained by Nicklès(3) in the reaction of ammonia upon cadmium, which was in contact with iron. He found, approximately, the composition HO, CdO.

Carbonate of Protoxide of Cadmium, of the composition $2(CdO, CO_2) + HO$, is obtained, according to Lefort(4), by adding an alkaline carbonate to a cadmium-solution. The water is expelled only between 80° and 120°.

Sulphate of Protoxide of Cadmium has been prepared by Kühn(5). It was deposited in hard crusts of an indistinct crystalline structure, from a solution containing an excess of sulphuric acid, and was found to contain $CdO, SO_3 + HO$; a basic salt of the composition $2\,CdO, SO_3 + HO$, was produced by decomposing a third of the solution of sulphate, by means of potassa, and continuously boiling the precipitate which was formed with the remainder of the solution.

Tin. Salts of Protoxide of Tin.—Bouquet(6) has examined several salts of protoxide of tin.—*Sulphate of protoxide of tin,* SnO, SO_3, crystallizes in small plates, from a hot saturated solution

(1) Ann. Ch. Pharm. LXIII, 279.
(2) J. Pharm. [3] XII, 61.
(3) Ann. Ch. Phys. [3] XXII, 31; J. Pharm. [3] XII, 406.
(4) Compt. Rend. XXVII, 268; J. Pharm. [3] XV, 20, (in detail).
(5) Arch. Pharm. [2] L, 286.
(6) From the "Recueil des Travaux de la Société d'Emulation pour les Sciences Pharmaceutiques," Janvier, 1847, 3, in J. Pharm. [3] XI, 459; Ann. Ch. Pharm. LXIV, 278, (in abstr.)

Tin. Salts of protoxide of tin.

of freshly precipitated protoxide of tin in dilute sulphuric acid. It is very soluble in water; the solution soon becomes turbid, a basic salt being deposited, which is redissolved by addition of a few drops of sulphuric acid. It forms crystallizable double compounds with the sulphates of potassa and ammonia; when ignited, binoxide of tin remains behind.—*Hyposulphate of protoxide of tin* can be obtained in solution only; when concentrated *in vacuo,* protosulphide of tin is separated.—*Tartrate of protoxide of tin,* 2 SnO, $C_8 H_4 O_{10}$, may be easily prepared by adding a boiling solution of tartaric acid to a concentrated solution of protoxide of tin in acetic acid, until crystallization commences; the crystals, which appear to be rectangular prisms, are soluble in water, which does not decompose them even at the boiling temperature; the solution is not precipitated by ammonia.—Protoxide of tin forms crystallizable double salts with the bitartrates of potassa and ammonia.—*Oxalate of protoxide of tin,* SnO, C_2O_3, is prepared like the tartrate; it forms brilliant needles, which are insoluble in cold water, and partially decomposed on ebullition. This salt dissolves in alkaline oxalates, double compounds being produced, which may be obtained, likewise, by treating alkaline binoxalates with hydrated protoxide of tin. The *potassa-double salt* SnO, $C_2 O_3$ + KO, $C_2 O_3$ + HO forms large crystals, which appear to belong to the rhombic system. The *ammonia-double salt* is isomorphous with the former; when heated it fuses and detonates.—The *soda-double salt* is anhydrous and crystallizable. All these double salts are soluble in water; the solutions becoming turbid after some time, and immediately on ebullition. Bouquet adduces that, in addition to the above, he has prepared the citrate, phosphate, and carbonate of protoxide of tin; he did not succeed in obtaining the acetate in the crystalline state.

Protochloride of Tin.—For preparing tin-salt (hydrated protochloride of tin) Nöllner(1) recommends to expose, in stone-ware receivers, granulated tin to the action of hydrochloric acid, as it is disengaged from the retorts, and to evaporate the concentrated solution of protochloride obtained in this manner in tin pans which are protected by granulated tin.

Binoxide of Tin.—R. E. Brown(2) has found that stannate of soda is formed by boiling a mixture of tin, carbonate of soda, and indigo, when the latter is dissolved; he farther states that the same salt is obtained by boiling a solution of soda with tin and protoxide of lead, metallic lead being separated.

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(1) Ann. Ch. Pharm. LXIII, 120. (2) Chem. Gaz. 1847, 60.

Stannic Acid and Metastannic Acid.—Fremy(1) had asserted that the two modifications of binoxide of tin, the normal one (stannic acid, obtained by the decomposition of the bichloride) and the anomalous one (metastannic acid produced by the action of nitric acid upon tin) have different equivalents, the former being represented by SnO_2, the latter by Sn_3O_6. This result had been obtained by the analysis of the potassa- and soda-compounds, which are formed by boiling metastannic acid with an alkali, and precipitating the solutions thus obtained by alcohol. He now finds that his former experiments were made with mixtures, the metastannates being on ebullition gradually converted into stannates. His new method of preparing metastannate of potassa, consists in dissolving metastannic acid in a cold dilute potassa-solution, and adding solid potassa, when the compound is separated as a white granular precipitate. When dried on a porous porcelain-plate, this precipitate is resinous and transparent; it is completely dissolved by water, an alkaline solution being formed which cannot be crystallized by evaporation; on addition of an acid a precipitate of metastannic acid (insoluble in nitric acid) is produced. Metastannate of potassa, when heated or left in contact for several days with an excess of potassa, is converted into stannate of potassa. According to Fremy, the salt dried at 130^0 contains KO, $Sn_5\ O_{10}+4\ HO$; when heated it loses its water and undergoes decomposition. The ignited salt yields to water, potassa and a small quantity of metastannic acid; 100 parts leave 79 parts of metastannic acid. Stannate of potassa does not lose its solubility by exposure to a red heat; the solution on addition of an acid deposits stannic acid, which is perfectly soluble in nitric acid. Stannic acid and metastannic acid.

Fremy prepared metastannate of soda by the action of a concentrated soda-solution on metastannic acid. The white, granular crystalline salt is very difficultly soluble in water. At as low a temperature as 60^0 (when dissolved by ebullition), it is decomposed into metastannic acid and soda. According to an approximative analysis, this salt contains $4\ H\ O$ to NaO, $Sn_5\ O_{10}$.

By his analysis of hydrated metastannic acid, Fremy was led to the formula $Sn_5\ O_{10}+10\ HO$; this analysis refers to a substance which was perfectly insoluble in ammonia, and which had been dried at the ordinary temperature in an anhydrous atmosphere. When dried *in vacuo*, this hydrate became $Sn_5O_{10}+5\ HO$, when exposed for several hours to a temperature of 130^0, it was converted into

(1) Ann. Ch. Phys. [3] XXIII, 393; J. Pr. Chem. XLV, 200.

Stannic acid and metastannic acid.

$Sn_5 O_{10} + 4 HO$, at 160° into $Sn_5 O_{10} + 3 HO$. The hydrate $Sn_5 O_{10} + 5 HO$ appeared to be of the greatest stability. The potassa- and soda-compounds, which have been mentioned, are formed by the substitution in this compound of one equiv. of alkali for one equiv. of water. (Stannic acid, to which Fremy assigns the formula $Sn O_2, HO$, when dried *in vacuo*, exhibits exactly the same percentage as the hydrate of metastannic acid in question). Metastannates, when precipitated with acids, yield metastannic acid, which is insoluble in nitric acid, but has the peculiar property of dissolving in ammonia.

The two modifications of binoxide of tin have been studied likewise by H. Rose(1). He calls *binoxide a*, the modification to which Fremy assigns the name of stannic acid, and which is obtained by precipitating with ammonia a solution of bichloride or hydrated bichloride of tin (the analysis of H. Rose confirms the formula of Lewy, who had found $SnCl_2 + 5 HO$ for this compound). Fremy's metastannic acid is designated by Rose *binoxide b*.

Binoxide *a* dissolves in cold hydrochloric acid, both dilute and concentrated. Binoxide *b* is insoluble in hydrochloric acid, even on application of heat; it dissolves, however, when heated with the acid upon addition of water.

The solution of bichloride of tin or hydrated bichloride (*i.e.* of binoxide *a*) is not precipitated by dilute sulphuric, hydrochloric, nitric, or arsenic acids; not even after some time. Phosphoric acid (tribasic, which precipitates the yellow silver-salt) produces, after some days, a colourless jelly. With arsenious acid a considerable precipitate is formed after some time. Only when diluted with a considerable excess of water, is the solution of bichloride of tin precipitated by dilute sulphuric acid; this precipitate is immediately redissolved on addition of hydrochloric acid.

The hydrochloric solution of binoxide *b* yields a strong precipitate on addition of dilute sulphuric acid, even in the presence of large quantities of hydrochloric acid; this precipitate contains both binoxide of tin and sulphuric acid, which latter can be removed completely by warm water, when binoxide *b* is left with its original properties; when treated with hydrochloric and nitric acids, it is dissolved after addition of water, the solution yielding after some time a strong deposit.—The solution of binoxide *b* in the smallest possible quantity of hydrochloric acid, is not affected by phosphoric

(1) Berl. Acad. Ber., June, 1848; Pogg. Ann. LXXV, 1; J. Pr. Chem. XLV, 76; Ann. Ch. Pharm. LXVIII, 272; Instit. 1848, 400; Chem. Gaz. 1848, 377.

acid; with arsenic acid, a copious white precipitate is formed after the lapse of 12 hours. Stannic acid and metastannic acid.

Both modifications *a* and *b* are precipitated on ebullition of their solutions in acids, especially in hydrochloric acid, when sufficiently diluted; binoxide of tin is thus perfectly separated, the more rapidly the smaller the quantity of free acid which is present. The precipitates produced both by ebullition and by addition of ammonia, are of the same modification as the binoxide which had served in the preparation of the solution.

Addition of tartaric acid prevents the precipitation by ammonia of the hydrochloric solution of binoxide *a*; with a solution of binoxide *b* this is not the case. The solutions of both modifications are precipitated by an excess of nitrate of protoxide of silver; the precipitate is perfectly soluble in an excess of ammonia if the modification *a* were in solution, while in the case of binoxide *b* the binoxide remains, chloride of silver only being dissolved.

Infusion of gall-nuts does not affect a solution of binoxide *a*, while in a solution of binoxide *b* a white-yellowish precipitate appears after some hours.

Carbonate of potassa produces in a solution of bichloride of tin (binoxide *a*), with effervescence, a very voluminous precipitate, which is completely soluble in an excess of the precipitant. The precipitate thrown down by carbonate of potassa in a solution of binoxide *b* is insoluble in an excess of the precipitant.

Both modifications, *a* and *b*, are soluble in solutions of potassa and soda; the solutions, when freshly prepared, contain the respective modifications with their peculiar properties. The solution of binoxide *b* in potassa, when mixed with an excess of potassa, yields a precipitate, which disappears on addition of water. When dried at 100°, this precipitate contains, according to Weber, $KO, Sn_7 O_{14} + 3 HO$.

Solution of bichloride of tin, which had been prepared six years, exhibited the reactions of binoxide *b*; in another specimen, which had been prepared only two years previously, the transformation had not been perfectly accomplished.

If so large a quantity of hydrochloric acid be added to a solution of bichloride of tin that it ceases to be precipitated on ebullition, the solution, after having been boiled for some time, shows the reactions of binoxide *b*; a solution of bichloride of tin, when mixed with potassa until the precipitate formed is perfectly redissolved, after standing for some time, exhibits the same deportment.

It is very probable that there are other modifications of binoxide of tin than *a* and *b*. In Rose's opinion, native binoxide of tin and

Stannic acid and metastannic acid.

ignited binoxide have to be considered as a peculiar modification, with which the product obtained by fusing binoxide of tin with alkaline carbonates, appears to be identical. Rose is not inclined to ascribe to different capacities of saturation the differences exhibited by the two modifications *a* and *b*.

Lead.—Lefort(1) states that the precipitate obtained by addition of an alkaline carbonate to a boiling lead-solution, contains 3 PbO, $2\,CO_2$, HO; the compound PbO, CO_2 could be obtained only by precipitating in the cold.

The precipitate obtained by addition of iodide of potassium to a solution of tribasic acetate of lead is, according to Kühn's(2) experiments, PbI + PbO + HO. Denot had assigned to it the formula PbI + 2 PbO. In a boiling solution of iodide of lead, ammonia produced a white precipitate, turning yellow when slightly heated, and approximating to the composition PbI + 3 PbO + HO. According to Kühn(3), freshly precipitated sulphate of protoxide of lead, when treated with ammonia, is converted into 2 PbO, SO_3.

Iron.—By treating cast iron with dilute sulphuric acid, Sandrock(4) did not obtain any compound which could have been designated as organic; the volatile products of this reaction were found to consist of hydrogen, arseniettcd and phosphoretted hydrogen, hydrosulphuric and sulphurous acid; the graphitic residue did not yield any humus-like body to potassa, which extracted sesquioxide of iron and silicic acid, the former being soluble in potassa by the cooperation of the latter.

The fact that iron is rapidly oxidized (with increase of volume) by the influence of saline solutions, especially of urine, has been established by observations of Persoz(5).

Carbonate of Protoxide of Iron.—Glasson(6) has ascertained that in the distillation of spathic iron (air being excluded) carbonic acid and carbonic oxide are evolved in nearly the proportion of 5 : 1, and that the residuary proto-sesquioxide of iron contains $Fe_2O_3 + 4\,FeO$.

Sesquioxide of Iron.—The spec. grav. of artificial sesquioxide of iron has been determined by H. Rose; when ignited over a spirit-lamp, it showed the spec. grav. of 5·17, while it was found to be 5·04 after exposure in a charcoal-fire. At the temperature of a porcelain-furnace the sesquioxide fused, but was found to have been

(1) Compt. Rend. XXVII, 268; J. Pharm. [3] XV, 26, (in detail.)
(2) Arch. Pharm. [2] L, 281. (3) Ibid. 284. (4) Ibid. LIV, 1.
(5) Ann. Ch. Phys. [3] XXIV 506; J. Pharm. [3] XV, 105.
(6) Ann. Ch. Pharm. LXII, 89; J. Pr. Chem. XLIV, 119, (in abstr.)

partially reduced to protoxide. According to G. Rose(1), the spec. grav. of the native sesquioxide (specular iron ore) is 5·19 to 5·23. Sesquioxide of iron.

Phosphate of Protoxide of Iron.—Iron nails found in the stomach of an ostrich, which were partly surrounded by black animal matter, when exposed for several days to the action of the atmosphere, exhibited peculiar blue stains, which Schlossberger(2) ascertained to be due to the presence of tribasic phosphate of protoxide of iron (vivianite).—The occurrence of crystallized *vivianite* in the bones of the skeleton of a miner, which had been found in an old mine of Tarnowitz, has been observed by Haidinger(3).

Sulphate of Protoxide of Iron.—The precipitate which deposits from a solution of sulphate of protoxide of iron, when exposed to the atmosphere, contains, according to Wittstein(4), when dried at 100°, $2\ Fe_2O_3, 3\ SO_3 + 8HO$; (Berzelius had adopted the formula $2\ Fe_2O_3, SO_3 + 6\ HO$).

Jacquelain(5) has announced the existence of three, hitherto unknown compounds of sulphuric acid with sesquioxide of iron; these compounds are $Fe_2O_3, 3\ SO_3 + 10\ HO$, (this is the formula of the mineral coquimbite), $Fe_2O_3, 4\ SO_3 + 12\ HO$, and $5\ Fe_2O_3, 32\ SO_3 + 26\ HO$. Details are still wanting.

Nickel. Protoxide of Nickel.—Genth(6) has more accurately determined the spec. grav. of crystallized protoxide of nickel, for which he had formerly obtained the number 5·745; according to his new experiments it is 6·605.

Carbonate of Protoxide of Nickel.—The apple-green precipitate produced by an alkaline carbonate in a cold nickel-solution, contains according to Lefort(7) $5\ NiO, 2\ CO_2 + 8\ HO$; the precipitate obtained with bicarbonates which has a similar colour, is $3\ NiO, 2\ CO_2 + 6\ HO$; the grass-green precipitate formed on ebullition was found to have the composition $5\ NiO, CO_2 + 5\ HO$; the same compound is obtained by boiling one of the preceding precipitates.

Copper.—Regarding the diffusion of copper, especially its existence in mineral waters, the reader is referred to the Report on Mineral Waters.

(1) Pogg Ann. LXXIV, 440; J. Pr. Chem. XLIV, 230; Berl. Acad. Ber. April, 1848; Instit. 1848, 369.
(2) Ann. Ch. Pharm. LXII, 382.
(3) Ber. der Freunde der Naturwissensch. in Wien, IV; J. Pr. Chem. XLIV, 181.
(4) Repert. Pharm. [3] I, 185. (5) Compt. Rend. XXIV, 441.
(6) Pogg. Ann. LXXIV, 439.
(7) Compt. Rend. XXVII, 268; J. Pharm. [3] XV, 21, (in detail).

Hydrated oxides of copper.

Hydrated Suboxide of Copper.—According to the experiments of Fremy(1), yellow hydrate of suboxide of copper (obtained by precipitating a solution of subchloride of copper in hydrochloric acid by means of carbonate of potassa or soda), is soluble in all acids, even the weakest, a salt of suboxide being produced. When rendered anhydrous, and even in the presence of water under conditions which are not sufficiently studied, it loses its basic properties and is decomposed by acids.

Hydrated Protoxide of Copper, when precipitated from a cold solution of the sulphate by a large excess of potassa and dried *in vacuo*, has been found by Fremy(2) to contain CuO + 2 HO.

Nitrate of Protoxide of Copper.—Gladstone(3) found in accordance with Graham's statements, that the prismatic nitrate of copper, which crystallises at 20^0, contains 3 equivs. of water (Gerhardt had found 4 equivs.) The basic salt obtained by heating the former, was found to contain 4 CuO, NO_5 + 3 HO, in conformity with Gerhardt's analysis. The same composition is assigned by Kühn(4) to a salt, which he prepared by incompletely precipitating with ammonia a cold solution of the neutral nitrate.

Mixed Vitriols.—Lefort(5) has examined several mixed vitriols of the composition CuO, SO_3 + 3 (FeO, SO_3) + 28 HO and CuO, SO_3 + 3 (ZnO, SO_3) + 28 HO. Nicklès(6), in studying the crystalline form of these compounds has confirmed the previously known fact, that it is the same as that of sulphate of protoxide of iron with very simple combinations.

Mercury.—Svanberg(7) has vainly tried several new methods for determining the equivalent of mercury; he has communicated details only respecting the decomposition of protochloride of mercury by means of lime at high temperatures, and in an atmosphere of hydrogen; he determined the amount of mercury obtained from a known weight of protochloride. He arrived in this manner at the numbers 99.79, 99·86 and 99·94; he believes, that these experiments prove, at all events, that the equivalent of mercury is not below this

(1) Ann. Ch. Phys. [3] XXIII, 391; J. Pr. Chem. XLV, 198.
(2) Ann. Ch. Phys. [3] XXIII, 388; J. Pr. Chem. XLV, 195.
(3) Chem. Soc. Mem. III, 480; J. Pr. Chem. XLIV, 179; Arch. Pharm. [2] LVII, 40.
(4) Arch. Pharm. [2] L, 283.
(5) Ann. Ch. Phys. [3] XXIII, 95; Compt. Rend. XXVI, 185; J. Pharm. [3] XIV, 15; J. Pr. Chem. XLV, 106.
(6) Ann. Ch. Phys. [3] XXIII, 104; J. Pr. Chem. XLV, 113.
(7) From the Memoirs of the Stockholm Academy for 1845, in J. Pr. Chem. XLV, 468; Chem. Gaz. 1849, 135 (in abstr.).

numoer. (Erdmann and Marchand had ascertained it to be 100·07). Mercury.

H. Kopp(1) found the spec. grav. of pure mercury at 0° to be 13·595 (water at 4° = 1); the experiments of Regnault(2) had given the number 13·596.

Mercury-Compounds.—Laurent(3) has published a synopsis of the formulæ, representing, according to his views, the various compounds of mercury. We cannot reproduce this synopsis, and limit ourselves to indicating the principle on which his classification is based. The mercury-compounds are considered as corresponding to simple compounds, f. i., of potassium or ammonium, in which certain equivalents are replaced by mercury. Mercury is stated to enter into combination with two different equivalents, representing as it were two different metals; the metal of the equivalent 100 is designated by the term *mercuricum,* while that of the equivalent 200 is called *mercurosum.* According to Laurent's view, a simple compound of ammonium may serve as type of many mercury-compounds, if we imagine 1 (sometimes also 1½) 2, 3 or 4 equivalents of hydrogen to be replaced by a corresponding number of equivalents of *mercuricum* or *mercurosum,* while arsenic or phosphorus is substituted for nitrogen; 1 equivalent of mercury can, however, be substituted for 1 equivalent of ammonium also. (The question arises, whether ammonium be capable of replacing the hydrogen in ammonium, when in the chemical acceptation of the term the whole becomes equal to part of it ?)

Deportment of Mercury-Solutions with Zinc. — H. Rose(4) finds that mercury is completely precipitated by zinc from the solution of the nitrate and the sulphate of the protoxide, provided the formation of basic salts be prevented by the addition of sulphuric or nitric acids. The mercury which is thus separated does not combine with the zinc. The same deportment is observed in the action of zinc upon protochloride of mercury. In the presence of hydrochloric acid, zinc forms an amalgam, and the last portions of mercury are precipitated only after a considerable time. The action of hydrochloric acid upon zinc is readily interrupted by the addition of protochloride of mercury, when amalgamation ensues at once. Dilute sulphuric and nitric acids produce the same effect in a solution of protochloride of mercury as hydrochloric

(1) Pogg. Ann. LXXII, 18.

(2) Ann. Ch. Phys. [3] XIV, 236; Relation, &c. (see p. 52), 158; Pogg. Ann. LXXIV, 210.

(3) Compt. Rend. XXIV, 222.

(4) Pogg. Ann. LXX, 311; Berl. Acad. Ber., January, 1847, (in abstr.); Ann. Ch. Pharm. LXIV, 273; J. Pr. Chem. XL, 308; Phil. Mag. [3] XXX, 290.

Deportment of mercury-solutions with zinc. acid.—Subchloride of mercury, even in the freshly precipitated state, and sulphate of the suboxide (when suspended in water), are not completely decomposed by zinc while, from a solution of the nitrate of the suboxide, the metal is perfectly separated.

Nitrate of Suboxide of Mercury.—Gerhardt(1) has examined the compounds of mercury with nitric acid. The vapour of hyponitric acid, when acting upon mercury, gives rise to the formation of nitrate of the suboxide, binoxide of nitrogen being evolved. He confirms the formula $Hg_2O, NO_5 + 2\,HO$ for this compound. On boiling this salt with a small quantity of water or nitric acid (the evaporated acid being replaced by water), a solution is obtained which deposits, on cooling, small brilliant oblique rhombic prisms, of the composition $2\,Hg_2O, NO_5 + HO$; by ebullition with a large quantity of water, a yellow salt is produced, which contains probably $3\,Hg_2O, NO_5$. The crystalline nitrate of the suboxide yields, on heating, a yellow salt, which is the basic compound, $Hg_2O, 2HgO, NO_5$, described by Brooks. Gerhardt denies the existence of the salt $6\,HgO, NO_5$, which has been mentioned by Kane.

Protiodide of Mercury.—According to Mohr's(2) experiments, the conversion of iodine and mercury into iodide, when moistened with alcohol and triturated together in equal equivalents, is not complete; the mass which is produced contains free iodine, which is evolved in the water-bath, and suboxide of mercury; by sublimation it is converted into protiodide and metallic mercury.

Decomposition of Subchloride of Mercury.—It has been observed by A. Vogel jun.(3), that subchloride of mercury, when heated with water and carbonate of lime (or carbonate of magnesia), is converted into suboxide of, and metallic, mercury, with formation of chloride of calcium (or chloride of magnesium), and evolution of carbonic acid. The carbonates of baryta and strontia, act in the same manner, but less energetically.—On ebullition of subchloride of mercury with powdered sulphate of lime, small quantities of chloride of calcium, and sulphate of suboxide of mercury are formed. Glauber's salt has the same effect.

Deportment of Chloramide of Mercury.—Kosmann(4) has examined the action of several acids and acid salts upon this compound (infusible white precipitate $HgCl + HgNH_2$). A solution obtained by boiling this substance with very dilute sulphuric acid, deposited

(1) Compt. Rend. XXVI, 432; J. Pharm. [3] XIII, 465.
(2) Arch. Pharm. [2] LV, 29.
(3) Repert. Pharm. [3] I, 34.
(4) J. Pharm. [3] XIV, 321; J. Pr. Chem. XLVI, 81.

on evaporation white foliated crystals of the formula $2(HgO, SO_3) + NH_4Cl + HgCl$, sulphates of ammonia and protoxide of mercury remaining dissolved. The crystals lost their HgCl by treatment with ether: under the influence of water they became yellow with formation of a basic sulphate.—Very dilute nitric acid, when cold, had but little action on the white precipitate, which was however dissolved on heating; on evaporation a copious crop of foliated crystals was deposited, presenting the lustre of metallic silver and containing $4HgCl + NH_4O, NO_5$; they were insoluble in water, and lost a large quantity of HgCl, when treated with ether. On farther evaporation the mother-liquid yielded small oblique prisms of metallic lustre, which were found to be a mixture of a little protochloride with a large quantity of nitrate of protoxide of mercury and ammonia.—Equal parts of the white precipitate, of chloride of sodium, and hydrochloric acid, when heated with 15 times their amount of water, yielded a solution which deposited, first, chloride of sodium, and then four-sided plates of metallic lustre, soluble in water, having the composition $2HgCl + NH_4Cl + 4NaCl$.—On boiling the white precipitate with double the weight of binoxalate of potassa in a sufficient quantity of water, carbonic acid was evolved, with formation of an insoluble residue of oxalate of suboxide of mercury; the solution, when exposed to solar irradiation, immediately deposited subchloride of mercury.—When the white precipitate was treated in a similar manner, with three parts of bitartrate of potassa, carbonic acid was likewise disengaged; the solution deposited, on cooling, several salts of different appearance, the composition of which was not sufficiently investigated.—On ebullition with acetic acid, subchloride of mercury was immediately precipitated with evolution of carbonic acid; the solution yielded, on evaporation, yellow crystalline crusts, which blackened on exposure to light, and contained 72·9 per cent of mercury, and 13·0 per cent of chlorine; Kosmann, considers them as an *acétate sexbasique de chlorure amido-mercurique* + 12 HO.—Treatment of the white precipitate with sulphate of quinine and very dilute sulphuric acid, gave rise to the formation of indistinct crystals which, after recrystallization from alcohol, are stated to have been 6 quinine, $12SO_3 + HgO, SO_3 + NH_4O, SO_3 + HgCl$.

Deportment of chloramide of mercury.

Silver.—L. Kessler(1) recommends to employ acetate of protoxide of iron for the purpose of precipitating metallic silver from solutions containing lead and copper; this salt effects a complete reduction,

(1) J. Pharm. [3] XI, 86.

Silver. while the sulphate invariably leaves small quantities of the metal in solution. Solutions, to be precipitated in this manner, should be very dilute, and as free as possible from an excess of acid.—A pure silver-solution, when precipitated by acetate of protoxide of iron, yields, according to Mohr(1), a dazzling white acetate, soon exhibiting dark spots, from which the reduction rapidly proceeds through the whole mass; from a solution containing copper and free nitric acid, the silver is at once precipitated in the metallic state. Of all the methods proposed for the decomposition of chloride of silver, Mohr considers the reduction by means of metallic zinc as most advantageous. With respect to Gregory's method, which consists in converting the chloride into oxide by boiling with a concentrated solution of potassa, he remarks, that frequently a portion of the chloride agglutinates, whereby the decomposition is prevented; he states that this may be best avoided by introducing the chloride, suspended in a small quantity of water into the boiling solution of potassa. He confirms the complete decomposition of chloride of silver by boiling with a solution of potassa and sugar, as communicated by Levol. By this method, the metallic silver could be easily obtained in dense and heavy masses, from which the liquid could be rapidly decanted.

According to Malaguti and Durocher(2), various sulphides and arsenides are capable of decomposing chloride and bromide of silver. The change takes place more rapidly if the silver-compounds are in solution than by contact under water only. They state that the decomposition takes place in the following proportions :

100 ZnS	3 AgCl;	100 BiS_3	2 AgCl;	100 SnS	½ AgCl;	100 Cu_2S	360 AgCl;
100 CdS	14 „	100 PbS	5 „	100 SnS_2	30 „	100 $SbAs_3$?	120 „

100 parts of arsenide of cobalt were found to decompose 166 of chloride of silver. The same compounds, when occurring as minerals, exhibited very different faculties of decomposition, according to the places in which they had been found. Bromide of silver was decomposed to a certain extent, iodide not perceptibly.

Chloride of Silver.—Pierre(3) has accurately determined the solubility of chloride of silver in hydrochloric acid. According to his experiments, one part of chloride of silver requires not more than

(1) Ann. Ch. Pharm. LXVI, 65; Arch. Pharm. [2] LIV, 15.
(2) Compt. Rend. XXV, 160; Arch. Pharm. [2] LIII, 321.
(3) From "Recueil des Travaux de la Société d'Emulation," (comp. p. 333), Avril, 1847, 107, in J. Pharm. [3] XII, 237.

200 parts of hydrochloric acid when concentrated, and not more than 600 parts when diluted with double its weight of water. Gold.

Gold.—According to C. T. Jackson(1), gold is obtained in the form of a yellow, soft sponge, by adding to a concentrated solution of gold a small amount of oxalic acid, and then a quantity of carbonate of potassa, sufficient to keep nearly the whole of the metal in solution, as aurate of potassa. On addition of crystals of oxalic acid and ebullition, the gold separates in the metallic state.

Teroxide of Gold.—Figuier(2) recommends as the best method for preparing teroxide of gold, to mix a solution of gold, from which, by repeated evaporation and re-solution the excess of acid has been removed as far as possible, with potassa, until the solution has a strongly alkaline reaction. To this solution chloride of barium is added, until the precipitate, which is yellow in the beginning, assumes a whitish colour. The precipitate of aurate of baryta is well washed, and decomposed by boiling for some minutes with dilute nitric acid, when teroxide of gold separates, which after washing must be protected from light whilst drying.

Sulphide of Gold and Sulphide of Potassium and Sodium.—Yorke(3) has examined the compounds of sulphide of gold with the sulphides of potassium and sodium. He found that a bright-red heat is necessary for producing these compounds from gold, alkali and sulphur; that if equal equivalents of gold and alkali be heated with three or four equivalents of alkali, about half the quantity of gold forms a compound soluble in water, and that the best proportions for obtaining the whole of the gold in the form of this soluble compound, are 1 equiv. of gold, 2 equivs. of alkali, and 8 equivs. of sulphur. By fusing gold with sulphur and soda, a product was obtained, yielding with water a yellow solution, which, when protected from oxygen during filtration, and evaporated over sulphuric acid *in vacuo*, deposited yellow crystals. These crystals, which became colourless on re-crystallization, belong to the monoclinometric system; they were six-sided prisms, exhibiting three or four terminal planes; when in contact with atmospheric air, they rapidly turned brown; when subjected to the action of heat, water, and afterwards sulphur, was evolved. The composition of this double salt is $AuS, NaS, + 8 HO$; it is soluble in water and spirits of wine; the solution yields with

(1) Sill. Am. J. [2] VI, 187.

(2) J. Pharm. [3] XII, 401; J. Pr. Chem. XLIV, 187; Ann. Ch. Pharm. XLIV, 295, (in abstr.)

(3) Chem. Soc. Qu. J. I, 236.

Sulphides of gold and sulphide of potassium and sodium.

acids a yellowish brown precipitate, whilst a small quantity of hydrosulphuric acid is evolved; the composition of the precipitate was found to vary, the quantity of sulphur present for 1 equiv. of gold oscillating between 1 and 2 equivs. In contact with air, the solution gradually decomposed and turned brown. Yorke obtained the same double salt by dissolving sulphide of gold, of nearly the composition AuS_2, (prepared by precipitation of the terchloride by hydrosulphuric acid), in sulphide of sodium, and crystallizing.—Sulphide of gold, when digested at the common temperature with hydrosulphate of sulphide of sodium is only sparingly dissolved; at a higher temperature, the sulphide of gold is reduced.—There exists likewise a compound of sulphide of gold and sulphide of potassium; this salt, however, is deliquescent, and crystallizes with difficulty. The solution exhibits the same deportment as that of the corresponding sodium-compound.

Glass containing Gold.—H. Rose(1) endeavours to explain the ruby colour which is exhibited by colourless glass containing gold, when it is heated. He assumes the existence in the colourless glass of a silicate of protoxide of gold, which requires for its formation a high temperature; when exposed to a gentle heat, part of the protoxide is separated, which produces the colour; when reduced to the metallic state by a higher temperature, it imparts a yellowish-brown colour to the glass, which at the same time loses its transparency. An analogous deportment is exhibited by glass coloured with suboxide of copper.

Platinum.—According to Pettenkofer's(2) observations, platinum is much more diffused, than was hitherto believed; all the silver which has not been obtained by direct processes of separation is stated to contain a small quantity of platinum.

J. Hess(3) recommends the following treatment of platinum ores. The ores are fused with 2 or 3 times their weight of zinc; the homogeneous brittle mass thus obtained, is powdered, sifted, and treated with dilute sulphuric acid, when most of the iron and zinc is extracted. The residue is then boiled with nitric acid, which removes iron, copper, lead, and sometimes palladium; and finally with aqua regia, in which it is easily soluble, on account of its high degree of comminution. The solution in aqua regia is separated as usual.

Blue Oxide of Platinum.—Platinum, when immersed into fused nitrate of potassa as the negative pole of a galvanic battery, forms,

(1) Berl. Acad. Ber., October, 1847; Pogg. Ann. LXXII, 556; J. Pr. Chem. XLIII, 75; Instit. 1848, 138; Ann. Ch. Pharm. LXIV, 288.

(2) Pogg. Ann. LXXIV, 316; Repert. Pharm. [2] XLVII, 72.

(3) Petersb. Acad. Bull. VI, 80; J. Pr. Chem. XL, 498; Ann. Ch. Pharm. LXIV, 267.

according to Hittorf(1), a blue oxide. He states, that the blue liquid which flows down the platinum, when separated from the metal, is rapidly converted into green and yellow oxide, which remain suspended in the nitrate of potassa; after cooling and absorbtion of moisture, the green oxide becomes yellow. In nitrate of soda the oxidation ensues less vigorously, the blue colour is brighter and more brilliant, the blue oxide which is formed gradually assumes a yellowish-brown colour.

Blue oxide of platinum.

Bisulphite of Protoxide of Platinum and Sulphite of Potassa.—Claus(2) has observed, that bichloride of platinum and potassium, when heated with sulphite of potassa, yields a colourless solution, from which, on evaporation, a white precipitate of the composition 3 $(KO, SO_2) + PtO, 2\ SO_2 + 2\frac{1}{2}\ HO$ is deposited. Hydrochloric acid reconverts it into bichloride of platinum and potassium.

Salts of Platinum-Bases and their Deportment.—Peyrone(3) had pointed out the existence of several compounds, which, having the same composition ($Pt\ NH_3\ Cl$) as the green salt of Magnus, are distinguished from this body by their physical properties; more recently he(4) has examined the deportment of these isomeric compounds with a solution of sulphite of ammonia; the analytical details of this investigation are still wanting, only the results having been communicated.—Peyrone states, that the green salt of Magnus, when boiled with an equal weight of sulphite of ammonia, was converted into a white powder $PtN_2H_7O_2, 2\ SO_2 + 2\ (PtNH_3O, SO_2)$ insoluble in alcohol and cold water, and scarcely soluble in boiling water. By continued ebullition with an excess of sulphite of ammonia, a solution was obtained from which alcohol precipitated drops of a viscid body, solidifying only after being for some time in contact with alcohol, and of variable composition. From the alcohol, used in precipitating the viscid body, white flakes were deposited after some time, having the composition $PtN_2H_7O_2, 2\ SO_2 + NH_4O, SO_2$.—The isomeric modification crystallizing in orange-yellow octohedrons was more readily attacked by sulphite of ammonia, two compounds being formed, namely, 1stly, a white powder insoluble in water having the same composition as the first substance produced in a similar manner from the salt of Magnus; and 2ndly, a substance, soluble in

(1) Pogg. Ann. LXXII, 481; J. Pr. Chem. XLII, 469, (in abstr.); Ann. Ch. Pharm LXIV, 248.
(2) Petersb. Acad. Bull. VI, 287; Ann. Ch. Pharm. LXIII, 357; J. Pr. Chem. XLII, 363; J. Pharm. [3] XIV, 394.
(3) Ann. Ch. Pharm. LI, 1; LV, 205. (4) Ibid. LXI, 178.

Salts of platinum-bases and their deportment.

every proportion in water, from which it was precipitated by means of alcohol in form of oily droplets, gradually solidifying and presenting the composition $PtN_2 H_7 O_2, 2 SO_2 + 2 (NH_4 O, SO_2)$.—The yellow modification, which may be obtained in large quantity, by gradually pouring at 13° small quantities of potassa into a solution of protochloride of platinum, neutralized by carbonate of ammonia, required, when thus prepared, 33 parts of water for solution. If boiled for a sufficient length of time with an excess of sulphite of ammonia, this modification was converted into small white needles of fatty lustre, containing $PtN_2 H_7 O_2, 2 SO_2 + 2 (NH_4 O, SO_2) + PtNH_3 Cl + HO$.—The yellow modification prepared by reduction, required 140 parts of water for solution; by boiling with sulphite of ammonia, an excess being avoided, transparent rhombic tables of a compound $PtN_2 H_7 O_2, 2 SO_2 + PtNH_3 Cl + 2 HO$, were formed, whilst ebullition with an excess of sulphite of ammonia gave rise to the formation of Böckmann's salt $PtN_2 H_7 O_2, 2 SO_2$.—The chlorine-compounds obtained by treating the above isomeric bodies with ammonia, were converted under the influence of sulphite of ammonia in the cold, into a substance crystallizing in four-sided prismatic transparent needles, scarcely soluble in cold, but soluble in 190 parts of boiling water, and containing, when dried at the ordinary temperature, $PtNH_3 O, SO_2 + PtN_2 H_6 O, SO_2 + 2 HO$. When boiled, the same chlorides yielded Böckmann's salt, ammonia being evolved.

Raewsky(1) has examined several compounds, which are also derived from the green salt of Magnus $PtNH_3Cl$. According to the temperature and concentration of the liquids, the latter was obtained of different colours, but of constant composition on adding ammonia to a hydrochloric solution of protochloride of platinum.—According to the statements of Gros, this compound, when treated with boiling nitric acid, is converted into metallic platinum, and a white crystalline salt $PtN_2H_6Cl O, NO_5$. Raewsky, on the other hand, finds that the separation of platinum is accidental, being due to the use of specimens of Magnus's salt, which have been partly decomposed by too much heat, and that the salt of Gros is formed only by the action of a small quantity of nitric acid. When treated with an excess of nitric acid, the green salt is stated to turn immediately brown, red vapours being evolved. If the liquid was boiled until

(1) Ann. Ch. Phys. [3] XXII, 278 (compl.); Compt. Rend. XXIII, 353, (in abstr.); XXIV, 1151; Ann. Ch. Pharm. LXIV, 309; LXVIII, 316; Gerhardt's Observations, J. Pharm. [3] XIV, 315.

Salts of platinum-bases and their deportment.

the latter ceased to be disengaged, when the conversion of the green salt was complete, the liquid deposited, on cooling, a white granular salt, which after repeated solution in warm water, and crystallization *in vacuo,* exhibited, when dried at 120°, the composition $Pt_2N_4H_{12}ClO_5$, $2\,NO_5$. The solution of this salt, when mixed with tribasic phosphate of soda, yielded (sooner or later, according to the use of boiling concentrated, or cold dilute solution) acicular tufts of a white salt, insoluble in cold, and hardly soluble in boiling water, and containing $Pt_2N_4H_{12}ClO_5, HO, PO_5$ when dried at 100°, while at 120° to 150° the water was lost. By decomposing the nitrate with oxalate of ammonia, a white granular powder, difficultly soluble, even in boiling water, was separated, which at 120° was represented by the formula $Pt_2N_4H_{12}ClO_5, 2\,C_2O_3$. Addition of carbonate of ammonia, to a solution of the nitrate, produced sooner or later, according to the concentration of the solution, a white precipitate, $Pt_2N_4H_{12}ClO_5, 2\,CO_2$ (at 120°). With hydrochloric acid, the nitrate gave a white granular precipitate soluble in water, which, at 120° was expressed by the formula PtN_2H_6ClO, Cl or $Pt_2N_4H_{12}Cl_2O_2, Cl_2$, clearly proving that this compound ceases to belong to the preceding series.

The mother-liquor obtained in the preparation of the nitrate of the preceding series, contains, according to Raewsky, another salt, which crystallizes only from very concentrated solutions. He states that, after repeated recrystallization *in vacuo,* it forms small brilliant needles, of the composition $Pt_2N_4H_{12}Cl_2O_4, 2\,NO_5$ (or $PtN_2H_6ClO_2, NO_5$.) Potassa-solution had no action upon this salt in the cold, when boiled, it assumed a yellow colour, a precipitate being formed, which, on ebullition, dissolved again with evolution of ammonia. A solution of silver produced no precipitate. The precipitate obtained by the action of hydrochloric acid upon the nitrate of the first series, might be considered as belonging to this second series.

By gradually adding bromine to a pretty concentrated and boiling solution of the compound PtN_2H_6Cl (either the yellow modification prepared according to Reiset's, or the colourless one obtained by Peyrone's method), a crystalline precipitate was immediately produced; an excess of bromine having been added and expelled again by ebullition, crystals were deposited, represented by the formula $PtN_2H_6Cl_2Br$, which proved that its formation is attended by no substitution. This compound was of an orange colour and nearly insoluble in cold water; with silver-solution it gave a precipitate of chloride and bromide of silver.

The action of chlorine upon a cold dilute solution of PtN_2H_6Cl gave rise to the formation of a yellowish compound, represented at

Salts of platinum-bases and their deportment. 120°, by the formula $PtN_2H_6Cl_2, HO$; while, in the boiling concentrated solution, the yellow chloride PtN_2H_6Cl, Cl of Gros's series, which is almost insoluble in water, was produced.

Palladium. Protochloride of Palladium and Ammonia.—From a memoir of N. W. Fischer(1) on palladium, we quote that the red modification of protochloride of palladium and ammonia $PdCl, NH_3$ is converted into the yellow one by solution in ammonia, and precipitation with hydrochloric acid; the yellow crystals, when dissolved in boiling hydrochloric acid and reprecipitated by ammonia, assume again the red colour.

Ruthenium. Sulphite of Protoxide of Ruthenium and Potassium.—Sesquichloride of ruthenium and potassium, according to Claus(2), is not dissolved in aqueous sulphurous acid at the common temperature, its colour only undergoes a superficial change to cream-yellow. A solution of this salt, when heated with sulphite of potassa, assumed a red colour, and deposited a cream-yellow precipitate. On evaporating to dryness, re-dissolving, and re-evaporating, an additional quantity of this precipitate was formed, the liquid retaining a deep orange colour. After repeated evaporations, and re-solutions, at last a nearly white precipitate remained, which was, however, not sufficient for examination. The cream-yellow compound was $KO, SO_2 + RuO, SO_2$.

Iridium. Sesquichloride of Iridium and Protochloride of Silver.—Claus(3) states, that nitrate of protoxide of silver produces in solutions of sesquichloride of iridium and potassium, a deep indigo-blue, flocculent precipitate, becoming paler after a few seconds, and ultimately colourless; the supernatent liquid is likewise colourless and free from iridium. The precipitate contains $Ir_2Cl_3 + 3\,AgCl$. It is insoluble in acids, in contact with strong ammonia a portion dissolves, while the other portion gradually assumes the form of (microscopic) rhombohedrons of diamond-lustre.—The above double compound is formed at once, without the production of the blue colour, if a boiling solution of the sesquioxide of iridium and potassium be employed.

Action of Sulphurous Acid and Sulphite of Potassa on Bichloride of Iridium and Potassium.—Claus has farther observed, that if finely powdered bichloride of iridium and potassium suspended in eight

(1) Pogg. Ann. LXXI, 431; Ann. Ch. Pharm. LXIV, 260, (in abstr.)
(2) Petersb. Acad. Bull. VI, 288; Ann. Ch. Pharm. LXIII, 359; J. Pr. Chem. XLII, 364; J. Pharm. [3] XIV, 394.
(3) Petersb. Acad. Bull. VI, 273; Ann. Ch. Pharm. LXIII, 337; J. Pr. Chem. XLII, 348; J. Pharm. [3] XIV, 385.

times the weight of water, be treated with a current of sulphurous acid, until a solution of an olive green colour is obtained, the bichloride is reduced to the state of sesquichloride, sulphuric and hydrochloric acids being formed; admixture of platinum, palladium, osmium, rhodium, and ruthenium are left undissolved. Neutralization of the free acid, with a concentrated solution of carbonate of potassa, produces at once an olive-green precipitate of small prisms, of diamond-lustre, which have the composition $Ir_2 Cl_3 + 3 KCl + 6 HO$. The same salt, but less easily, is obtained by exposing to a dull redness, bichloride of iridium and potassium or a mixture of this salt with $\frac{1}{3}$ its weight of carbonate of potassa, and extracting the product of fusion with water.—The crystallized salt rapidly effloresces in dry warm air, it is easily soluble in water, but insoluble in spirits of wine; the alkalies decompose it only with difficulty. Addition of nitrate of protoxide of silver to the aqueous solution precipitates at once $Ir_2 Cl_3 + 3 Ag Cl$.—The solution of bichloride of iridium and potassium, reduced by means of sulphurous acid, and from which the largest quantity of the above salt has been precipitated by carbonate of potassa, retains the olive-green colour at the ordinary temperature, when heated for some time, it turns red, and afterwards bright yellow, various compounds being formed, of which mixtures are obtained on evaporation or addition of water to the concentrated solution. They can be purified only with difficulty; Claus succeeded in isolating a rose-red crystalline salt, an amber-yellow compound of turpentine consistency, and a white powder, all containing potassa, sulphurous acid, chlorine and protoxide of iridium; they are difficultly soluble in water, and evolve, when strongly heated, sulphurous acid; in hydrochloric acid they are pretty soluble with disengagement of sulphurous acid, easily soluble crystalline salts being formed.

Action of sulphurous acid and sulphite of potassa on bichloride of iridium and potassium.

The red salt is prepared by dissolving one part of $Ir_2 Cl_3 + 3 KCl + 6 HO$ in 12 parts of water, adding $\frac{1}{2}$ a part of carbonate of potassa, perfectly saturating with sulphurous acid, and heating in a porcelain dish until the olive-green colour is changed to red; the solution deposits, after some days, small flesh-coloured or minium-red prisms, which are partly decomposed when re-dissolved in water. These crystals are more soluble in potassa than in water; the solution, bright-red in the cold, assumes a dark green colour on heating, which turns again yellow on addition of nitric acid (a small quantity of a white precipitate being formed). The crystals contain water, which is disengaged at 180^0; when dried in the air, they are $Ir_2 Cl_3, 4 (KO, SO_2) + 12 HO$. This salt dissolves with a yellow colour in

Action of sulphurous acid and sulphite of potassa on bichloride of iridium and potassium.

hydrochloric acid; on concentration, sulphurous acid is disengaged, the solution assuming a red colour, and depositing deep-red prisms of diamond-lustre, which turn opaque and yellow when moistened with water. The red prisms dissolve in water with a yellow colour, but are insoluble in alcohol; they contain water of crystallization, which is disengaged only with difficulty at 180°; their composition is represented by the formula $Ir_2 Cl_3$, 2 KO, 2 SO_2, 2 KCl + 4 HO; Claus is inclined to consider both the two preceding compounds and the following body as salts of protoxide of iridium with a peculiar acid, $S_2 O_4$ Cl.—The purification of the amber-yellow, turpentine-like compound is extremely difficult. Claus succeeded several times, by evaporating to a very small volume the mother-liquor of the former of the two red salts previously mentioned, decanting from a mixture of a white and red salt (*vide infra*), which is deposited, concentrating still further, and adding a considerable quantity of water; a whitish-yellow, flocculent precipitate is formed, which collects at the bottom of the vessel as a dingy-whitish viscid mass. It is dissolved by ebullition, and the solution filtered whilst hot, when the compound separates after some days as a beautiful amber-yellow, transparent, turpentine-like mass, dessicating to an amorphous, brittle, transparent substance, which yields an olive-yellow powder; this compound contains 2 IrO, 4 KO, 6 SO_2, Cl.—The formation of the preceding compound is attended by that of a white salt; it is obtained, though always in small quantity only, by adding a considerable quantity of sulphite of potassa to the solution from which the former of the above red salts has been deposited, and evaporating to a small bulk, when the white powder is precipitated, which has to be washed, until the precipitate produced in the washings by chloride of barium, is perfectly soluble in hydrochloric acid. The white powder is insoluble in water, slightly soluble in potassa; it contains 3 (KO, SO_2) + IrO, 2 SO_2 + 5 HO; dried at 180° it becomes anhydrous. Hydrochloric acid dissolves it with a yellow colour; the solution deposits pale-yellow prisms, easily soluble in water, and containing 3 KCl + IrO, 2 SO_2.

Osmium. Bisulphite of Protoxide of Osmium and Sulphite of Potassa.—Finely divided bichloride of osmium and potassium, according to Claus(1), is not affected by sulphurous acid in the cold; on heating, however, decomposition takes place; the solution assumes a dark green colour, black binoxide of osmium being separated, and deposits

(1) Petersb. Acad. Bull. VI, 285; Ann. Ch. Pharm. LXIII, 355; J. Pr. Chem. XLII, 361; J. Pharm. [3] XIV, 392

after filtration, upon cooling, unaltered bichloride of osmium and potassium. A solution of this salt, when heated with sulphite of potassa, turns at first dark-, afterwards bright- rose-red, and ultimately colourless, a white powder being precipitated, which is difficultly soluble, and undergoes decomposition at 180°, when it becomes dingy violet. When dried at 100°, this powder contains $3 (KO, SO_2) + OsO, 2 SO_2 + 5 HO$. Hydrochloric acid converts it into a brown-red crystalline salt, $3 KCl + OsO, 2 SO_2$, which is easily soluble. In cases of poisoning by osmic acid, Claus recommends the immediate inhalation of hydrosulphuric acid.

Osmium. Bisulphite of protoxide of osmium and sulphite of potassa.

Osman-Osmic Acid.—Fritzsche and Struve(1) have communicated the investigation of an acid containing osmium, nitrogen, and oxygen, which they consider as osmic acid conjugated with nitride of osmium, and for which they have proposed the term osman-osmic acid. In the formation of a nitride of osmium, OsN, a decomposition should ensue between OsO_4 and NH_3; Fritzsche and Struve have no notion what becomes of the fourth equivalent of oxygen(2).

The new acid is formed by the action of ammonia on osmic acid; the potassa-salt is easily formed by addition of ammonia to a solution of osmic acid in excess of potassa; the deep orange-yellow colour of the solution becomes bright yellow, when the newly formed salt is deposited as a bright yellow crystalline powder, either at once, or on evaporation at a gentle temperature. Osmic acid and ammonia give rise to the formation of the new acid also without the presence of potassa, but as the ammonia-salt is readily decomposed on evaporation, it is advisable to add bases, such as potassa, or protoxides of zinc and silver, which form more stable, and less soluble compounds. The salts of this acid, with the exception of the salt of suboxide of mercury, detonate on heating. The acid may be separated from the baryta-salt by dilute sulphuric acid, from the silver-salt, when still moist, by dilute hydrochloric acid; it forms a bright yellow solution, which, when dilute, may be kept unchanged for several days; when concentrated, however, it rapidly turns brown, with evolution of gas, liberation of osmic acid and separation of a black compound containing osmium. An aqueous solution of osman-osmic acid decomposes the carbonates, and even chloride of potassium; it dissolves metallic zinc with a slight evolution of gas, being itself partially

(1) Petersb. Acad. Bull. VI, 81; J. Pr. Chem. XLI, 97; Ann. Ch. Pharm. LXIV, 263 (in abstr.); J. Pharm. [3] XII, 304.

(2) This difficulty induced Gerhardt to adopt the formula, $Os_2 O_5 N$, (J. Pharm. [3] XII, 304).

Osman-osmic acid. decomposed. Sulphuric, nitric, and hydrochloric acid, do not act upon osman-osmic acid in the cold; when heated the solution turns brown, osmic acid being liberated.—The potassa-salt is prepared either as indicated, or by dissolving solid osmic acid in a mixture of ammonia and concentrated potassa-solution, when it is deposited as a granular precipitate at the same rate as the acid dissolves. This salt is deposited from a saturated solution in boiling water, in form of square-prismatic crystals P. 2 P ∞ ; principal axis for P = 1·1335; lateral edges = 116^0 5′; terminal edges = 106^0 16′. The composition of this salt is KO, (OsN, OsO_4); it may be heated to 180^0, when it slightly darkens; at a higher temperature it detonates. In the reaction of concentrated hydrochloric acid upon this salt, chlorine or an oxide of chlorine is evolved, the solution assumes a beautiful purple-red colour, while the crystals of the original salt are coated with a layer of two kinds of small red crystals, the formation of which increases until the original salt has perfectly disappeared. A cold saturated solution of osman-osmiate of potassa is not decomposed by dilute hydrochloric acid. On being heated the solution exhibits a transient red colouration, and then turns brown, with evolution of osmic acid; when boiled until this evolution ceases, and evaporated to crystallization, a red salt and two green salts are deposited, the one crystallizing in needles, the other in six-sided tables; all these salts appear to be decomposed upon re-solution in water, and could not be examined more minutely.—Osman-osmiate of soda, prepared by decomposing the silver-salt with chloride of sodium, is easily soluble, and crystallizes from the syrupy solution in crystals of considerable size, which contain water of crystallization. —The ammonia-salt, obtained by treating the silver-salt with chloride of ammonium, forms large crystals apparently isomorphous with those of the potassa-salt; they are easily soluble in water and alcohol, and detonate at 125^0.—The baryta-salt was prepared in a similar manner, by decomposing the silver-salt with chloride of barium; the solution, when evaporated over sulphuric acid, deposits yellow brilliant crystals, which are easily soluble in water, and detonate at 150^0; composition BaO, (OsN, OsO_4).—The zinc-salt, which is easily soluble, was not fully examined; it forms a compound with ammonia, which is obtained by dissolving osmic acid in an ammoniacal solution of a zinc-salt, or by adding a zinc-salt to an ammoniacal solution of osmic acid, when a bright-yellow crystalline powder is separated after a very short time, which is permanent in the air, but decomposed by water. Dried in the air its composition is ZnO, (OsN, OsO_4) + 2 NH_3. Cadmium exhibits an analogous

deportment.—On addition of nitrate of protoxide of lead to an alcoholic solution of the potassa- or ammonia-salt a yellow crystalline precipitate is obtained, which darkens during washing, and contains probably 2 Pb O, (OsN, OsO_4). Acetate of protoxide of lead produces with the osman-osmiates, a precipitate, which, at first dingy yellow, turns purple-red after some time; a solution of protochloride of lead yields with osman-osmiate of potassa a yellow crystalline precipitate, containing equal equivalents of osman-osmiate and protochloride of lead. The salt of suboxide of mercury is obtained as a bright-yellow amorphous precipitate upon mixing the potassa-salt with nitrate of suboxide of mercury; by application of a gentle heat it may be volatilized.—By decomposing the silver-salt with protochloride of mercury a solution is obtained, depositing after some time prismatic crystals which are rapidly blackened with liberation of osmic acid.—Osman-osmiate of protoxide of silver $AgO, (OsN, OsO_4)$ is prepared by dissolving osmic acid in an ammoniacal silver-solution, and adding an excess of nitric acid, or by mixing an ammoniacal solution of osmic acid, first with excess of nitric acid, and then with a silver-salt, or lastly, by precipitating a soluble osman-osmiate with nitrate of protoxide of silver; osman-osmiate of protoxide of silver is a yellow crystalline powder rather difficultly soluble in water and cold nitric acid, readily soluble in ammonia; even when protected from light it blackens after some time; it detonates at 80^0 and by percussion. Osman-osmic acid.

ORGANIC CHEMISTRY.

Generalities. Influence of time on the formation of chemical compounds.

Generalities. Influence of Time on the Formation of Chemical Compounds.—Liebig(1) has investigated the influence of time on the formation of chemical compounds. Alcohol, saturated with oxalic acid, deposits on cooling a portion of the acid in crystals; if the solution be exposed for some time to a temperature of 40° to 50°, the quantity of crystals deposited on cooling is gradually diminished, and after the lapse of several months the solution altogether ceases to crystallize on cooling. Long before this point is reached, considerable quantities of oxalic ether, and oxalovinic acid, may be traced in the liquid, and the amount of the former ultimately increases to such an extent, that it may be separated by addition of water. In a similar manner, hippuric acid and alcohol, give rise to the formation of hippuric ether. Benzoic acid is not etherified by alcohol alone; the transformation, however, ensues on addition of a few drops of fuming hydrochloric acid, or of alcohol saturated with hydrochloric acid gas. The formation of acetic and œnanthic ethers, in old wines, appears to take place in a similar manner.

Fermentation and Putrefaction.—A memoir has been published by Liebig(2) which treats of fermentation, and allied phenomena.

We point out the following of his views and observations. Liebig calls *putrefaction* every process of decomposition which, caused by external influences, in any part of an organic compound, proceeds throughout its entire mass without the farther co-operation of the original cause; *fermentation*, according to his definition, is the decomposition exhibited in the presence of putrefying substances, or ferments, by compounds, nitrogenous or non-nitrogenous, which alone are not capable of putrefaction. He distinguishes, in both putrefaction and fermentation, processes in which the oxygen of the

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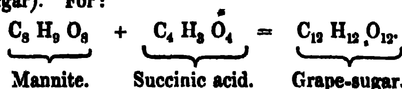
(1) Ann. Chem. und Pharm. LXV, 350.
(2) Liebig, Poggendorff, and Wöhler's Handwörterbuch der Chemie, III, 217.

Fermentation and putrefaction.

atmosphere continually co-operates, from such as are accomplished without farther access of atmospheric air. In lactic fermentation (of sugar with chalk and cheese), mannite(1) invariably is produced as a secondary product, the formation of which is not explained: it may be obtained by precipitating the mother-liquor of the lactate of lime by means of oxalic acid, evaporating the acid liquid to syrupy consistence, and treating the residue with boiling alcohol, when, on addition of ether, mannite is separated. A solution of leucine, when in contact with the atmosphere, is rapidly decomposed upon addition of a trace of putrefying fibrin; the solution contains a considerable quantity of valerianate of ammonia. Leucine does not undergo decomposition without the addition of putrefying fibrin.—Fibrin, when covered with a thin layer of water, and exposed to the atmosphere until putrefaction is accomplished, is found to be converted into a fluid, which exhibits the deportment of a solution of albumin; on ebullition a coagulum separates, possessing the colour and all the properties of coagulated white of egg.

Liebig opposes the view, which considers putrefaction and fermentation as the result of vital processes, f. i., of the development of vegetal formations, or of microscopic animals: he adduces, that no traces of vegetal formations are perceptible in milk, which is left for some time in vessels carefully tied over with blotting-paper, not even after fermentation has regularly set in, a large quantity of lactic acid having been formed. He farther remarks, that of fermentative processes, alcoholic fermentation having been studied too exclusively, the phenomena observed therein had been generalized, while the explanation of this process ought to be derived rather from the study of fermentative phenomena of a more general character. Liebig communicates that some experiments have been made by Trautschold respecting the faculty exhibited, according to observations of Brendecke(2), by porous substances (straw, paper, charcoal, flowers of sulphur, &c.), of inducing alcoholic fermentation in a grape-sugar-solution, to which some tartrate of ammonia has been added. Fermentation observed under the circumstances adduced, is due to the

(1) The formation of mannite is, perhaps, connected with the production of succinic acid, which Schmidt, in a letter to Liebig, states that he has found in fermenting liquids (containing sugar). For:



$$\underbrace{C_8\,H_9\,O_8}_{\text{Mannite.}} + \underbrace{C_4\,H_3\,O_4}_{\text{Succinic acid.}} = \underbrace{C_{12}\,H_{12}\,O_{12}.}_{\text{Grape-sugar.}}$$

(2) Arch. Pharm. [2] XL, 10; Berzelius' Jahresbericht, XXV, 741; XXVI, 728.

Fermentation and putrefaction.

presence, in the sugar-solution, of a foreign substance, which may be removed by treating it with ignited bone-black. After repeated treatment in this manner, solution of grape-sugar, with or without the addition of tartrate of ammonia, ceases to ferment under the influence of one of the afore-mentioned porous substances. On the other hand, the bone-black, from which the sugar has been only partially removed, exhibits alcoholic fermentation at 18° to 20°.

Another memoir on fermentation in general has been published by Blondeau(1). He propounds the view, that every kind of fermentation is caused by the development of fungi. Blondeau states, that alcoholic fermentation is due to a fungus, which he denotes *Torvula cerevisiæ;* whilst another, *Penicillium glaucum,* gives rise to lactic fermentation. The latter fermentation follows the former in a mixture of 30 grm. of sugar, 10 grm. of yeast, and 200 c.c. of water, which has undergone alcoholic fermentation at a temperature of about 20°, being terminated in about two days. Beer-yeast, when left in contact with water in a dark and moist place, contains, according to Blondeau, germs both of *Torvula cerevisiæ,* and of *Penicillium glaucum;* the former can be separated by a filter, and will induce alcoholic fermentation in sugar-water, whilst the latter are extremely minute, and pass through the filter: the filtrate, mixed with sugar-water, gives rise to lactic fermentation. Acetic fermentation is due to the development of *Torvula aceti;* sugar is converted into acetic acid, without evolution of gas, if 500 grm., dissolved in a litre of water, be mixed with 200 grm. of casein, and confined in contact for a month at a temperature of about 20°. The conversion of nitrogenous substances into fat (f. i., of casein, in the manufacture of Roquefort cheese; of fibrin, under similar circumstances), which Blondeau designates by the term fatty fermentation (*fermentation adipeuse*), is caused by *Penicillium glaucum,* or *Torvula viridis;* and the former fungus is stated to act likewise in butyric and in urea-fermentation (conversion of urea into a carbonate of ammonia).

C. Schmidt(2) has communicated the following results of his experiments on fermentation. Urea, when in contact with yeast, is rapidly converted into carbonic acid and ammonia. In the presence of a small quantity of sugar, the transformation of urea commences only after the decomposition of the sugar. If yeast and sugar be used in a certain proportion, a sort of equilibrium is

(1) Journ. Pharm. [3] XII, 244, 336. (2) Ann. Ch. Pharm. LXI, 168.

Fermentation and putrefaction.

established; in the presence of a large quantity of sugar, urea is protected against decomposition, which ensues, however, on diminution of the sugar,—more or less rapidly, according to the excess of ferment present. A certain amount of yeast decomposes only a certain amount of urea. Schmidt observed that a given quantity of yeast, when brought into contact with the same amount of water, and varying quantities of urea, gave rise, during a given space of time, to the same amount of ammonia. The development of fungi is not required for the induction of urea-fermentation. A solution of gelatine, when mixed with urea, phosphate of soda, and sulphate of magnesia, filtered, heated to ebullition for half an hour, and then exposed to a current of atmospheric air, which had been passed through sulphuric acid, gave, after the lapse of eight days, the same amount of phosphate of magnesia and ammonia, as a similar liquid, *cæteris paribus*, when in contact with common atmospheric air. Nor are fungi the *primum movens* of saccharic fermentation: the clear filtrate, obtained by throwing almonds crushed in water upon a moist filter, soon induces fermentation in a solution of urea and of grape-sugar; in the latter case, no trace of ferment-cells can be discovered under the microscope, not even after fermentation is fully developed. If the solution, still containing sugar, is allowed to stand eight days, or a fortnight, after fermentation has ceased, an exuberant development of cellular aggregations is observed, but no putrefaction ensues: the fungi, well washed, and introduced into a fresh solution of grape-sugar, continue to grow luxuriantly, inducing, however, if at all, but very weak fermentation, which rapidly ceases; hence the growth of fungi during fermentative processes, is but a secondary phenomenon. The increase of the residuary ferment, which occurs after yeast has been in contact with sugar, arises from a development of ferment-cellulose, which probably takes place at the expense of the sugar. If muscle, gelatine, yeast, &c., in a very advanced state of putrid decomposition, be introduced into a solution of 1 sugar in 4 water, all phenomena of putrefaction disappear: after a few hours, active fermentation sets in, ferment-cells being formed, and the liquid contains alcohol, but no mannite. The inactivity of crushed yeast is due, not to the destruction of the fungi, but to the chemical changes which are induced in yeast during the considerable time necessary for complete comminution. The crushed cells, introduced into sugar-water, give rise to the production of lactic acid, without evolution of gas. Schmidt is of opinion, that fermentation is a process analogous to the formation of ether. He believes, that one of the constituents of

Fermentation and putrefaction.

yeast, together with the elements of grape-sugar, gives rise to the formation of one or several compounds, which are decomposed in *statu nascenti*, (like sulphovinic acid), splitting into alcohol and carbonic acid.

R. Wagner(1) also has communicated some remarks on the nature of yeast. He observed that the cells of upper yeast are chiefly distinguished from those of lower yeast, by being incontinuous.—He repeated the experiments which have been made on the propagation of yeast, and confirms for the case of upper yeast, that it takes place by the expansion of the cellular shell, and that the propagation of a newly-formed cell is possible only after a nucleus having been formed in its interior, which, however, is not derived from the mother-cell. He assumes, that the propagation of lower yeast takes place by the escape of the new cells from the mother-cell, although he did not succeed in directly observing it. Upper yeast, when brought into contact with beer-wort, at a temperature of 7°, is converted into lower yeast to a considerable extent, whilst no formation of upper yeast could be observed after addition of beer-wort to lower yeast at 20°. Upper yeast, when exposed in a watch-glass to the atmosphere, exhibits the vegetations observed by Kützing(2); these gradually pass into *Sporotrichum*, and, lastly, into *mucor*. Lower yeast, under the same circumstances, is at once converted into *Mucor*. Schmidt's observation (page 359), that the filtrate of almonds crushed in water induces the fermentation of grape-sugar, without giving rise simultaneously to the formation of ferment-cells, has not been corroborated by Wagner. In his experiments, evolution of carbonic acid, and formation of ferment-cells, invariably ensued at the same time. Nor does Wagner agree with Schmidt's statement, that washed ferment-fungi continue to grow when introduced into a fresh solution of grape-sugar, inducing either none or only weak and transient fermentation. He enquires whence the protein-substance necessary for the vegetation of the yeast, could have been derived in this case.—He farther examined, in what manner the faculty in yeast of inducing fermentation in a solution of grape-sugar in malt-extract, is affected by various agents. Yeast, dried at 100°, and powdered, ceased to exhibit, under the microscope, the form of cells, and induced fermentation only, after thirty-six hours. Small quantities of strong mineral acids prevent fermentation, with the exception, however, of

(1) J. Pr. Chem. XLV, 241. (2) Ibid. XI, 390.

Fermentation and putrefaction.

phosphoric acid, which appears to favour it. The effect produced by organic acids is variable: butyric acid seems to act by transforming alcoholic fermentation, probably induced previously, into butyric,—common yeast being converted into butyric acid ferment. Small quantities of acetic, tartaric, and especially lactic acid, exert the most favourable influence on the propagation of the ferment-cells. Fermentation is interrupted by even dilute solutions of alkalies, of soaps, and of chloride of lime, but is not affected by dilute solutions of quinine and strychnine, nor by small quantities of free sulphurous acid. Yeast is destroyed by sulphate of protoxide of iron, or of zinc, and by protochloride of mercury, but resists the action of sulphate of protoxide of copper, arsenious acid, and tartar emetic. Lastly, Wagner analyzed yeast prepared according to Schlossberger's(1) method (washing, pressing through linen, and exhaustion by alcohol and ether), and dried at 100°. He obtained the following average results corresponding with those of Schlossberger.

	Carbon.	Hydrogen.	Nitrogen.	Oxygen.	Ash.
Upper yeast .	44·37	6·04	9·20	40·39	
Lower yeast .	49·76	6·80	9·17	28·97	5·29

Finally, experiments on putrefaction and fermentation have been performed by Döpping and Struve(2). They do not confirm the results of Helmholz(3), who states that organic substances (grape-sugar, gelatine-solution, flesh, &c.), may be secured against putrefaction, when heated with water until ebullition ensues, if the vessel be closed so as to allow the access of ignited air. Döpping and Struve find, that all [illegible]enous organic substances undergo decomposition even under the influence of ignited air, but that the phenomena are only retarded and changed by the effect of ebullition. Helmholz had observed that the fermentation of grape-juice is not communicated to another portion of grape-juice which is contained in a vessel closed by bladder and introduced into the fermenting liquid. In repeating this experiment, Döpping and Struve once remarked a slight evolution of gas in the confined sugar-solution, and afterwards also the formation of ferment-cells, whilst the surrounding liquid was in a state of fermentation; in other experiments, however, this could not be observed again.

(1) Ann. Chem. Pharm. LI, 193.
(2) Petersb. Acad. Bull, VI, 145; J. Pr. Chem. XLI, 255.
(3) J. Pr. Chem. XXXI, 429; Berzelius' Jahresbericht, XXV, 805. At an earlier period, Schwann had obtained similar results.

Fermentation and putrefaction.

Nor do they corroborate Gay-Lussac's statement, that grape-juice, expressed with exclusion of air, is protected from fermentation, which ensues, however, after the access of a small quantity of oxygen. The atmospheric air was expelled in various ways, by hydrogen and by carbonic acid, from the vessel in which the grapes were pressed; fermentation, however, invariably took place. They are inclined to explain this discrepancy by a different space of time having elapsed between collecting and pressing the grapes, which might have influenced their subsequent deportment. Brendecke's statements (comp. p. 357) were confirmed so far as by the introduction of porous substances, both with and without tartrate of ammonia, phenomena of fermentation were induced in a solution of grape-sugar; they could not, however, trace any alcohol in the fermented liquid, but observed the formation of an acid.

Cyanogen and Cyanogen-Compounds. Cyanogen and Paracyanogen.—H. Delbrück(1) has performed some experiments on the important subject of the formation of cyanogen. He confirms the statements of Desfosses and Fownes, inasmuch as a weak but distinct formation of cyanogen was observed on igniting sugar-charcoal with carbonate of potassa in an atmosphere of nitrogen. Cyanide of potassium was moreover obtained by passing binoxide of nitrogen over the compound of potassium and carbonic oxide in a state of ignition, or by fusing potassium in an atmosphere of carbonic acid and ammonia, or of carbonic acid and nitrogen, and lastly by fusing potassium with pieces of carbonate of ammonia.(2)

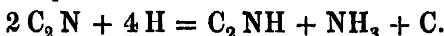
Paracyanogen, according to Delbrück, can be prepared in a state of purity only by heating dry cyanide of [illegible] acid, and If hydrocyanic acid be passed into a solution of cyan[illegible]e ti[illegible]um, or if a small amount of sulph[illegible] acid be added t[illegible] [illegible]trated solution of this salt, a brown [illegible]ogen-like bod[illegible] produced in considerable quantity. In [illegible]radiction to H. Thaulow and in accordance with Liebig, Gmelin, and Rommelsberg, the gas evolved on heating cyanide of silver, was found in no way differing from ordinary cyanogen; the residuary paracyanide of silver, when powerfully ignited, is decomposed into metal, which retains a small and varying amount of carbon, and a mixture of 1 vol. of nitrogen and 1·66 vol. of cyanogen. It contains no mellonide of silver, inasmuch as no mello-

(1) J. Pr. Chem. XLI, 161; Ann. Ch. Pharm. LXIV, 296.

(2) Possoz and Boissière, as will be mentioned in our Report on Technical Chemistry, have founded a process of manufacturing ferrocyanide of potassium upon the formation of cyanogen at the expense of atmospheric nitrogen.

nide of potassium is produced by fusion with sulphocyanide of potassium. Paracyanogen prepared from cyanide of mercury or silver, is not changed by nitric acid, while the brown substance formed by the action of cyanide of potassium on hydrocyanic acid is partly soluble therein; the solution is partially precipitated by water, more completely by salts of protoxide of silver or of lead and by ammonia. If a solution of paracyanogen in nitric acid be evaporated to dryness, the residue being gently heated, it is converted into a pale yellow substance, which is soluble in nitric acid and reprecipitated by water. Cyanogen and paracyanogen.

On heating cyanide of mercury, only about $\frac{1}{11}$ of its cyanogen remains as paracyanogen, which when ignited in a current of carbonic acid or nitrogen, is converted into pure cyanogen; other paracyanogen-bodies leave, under these circumstances, a small quantity of carbon. On ignition in hydrogen, hydrocyanic acid and ammonia are evolved with deposition of carbon:



$$2\,C_2N + 4\,H = C_2NH + NH_3 + C.$$

Paracyanogen, when heated in dry chlorine gas, gives rise to the formation of solid chloride of cyanogen. In one instance, a white substance was solidified, which was soluble in water, and in which the presence of cyanogen and chlorine could be traced only after fusion with carbonate of soda. Sulphur is without action on paracyanogen.

Hydrocyanic Acid.—Mohr(1) has shown that on distilling 1 part of ferrocyanide of potassium, ½ part of sulphuric acid, and the proper quantity of water, to dryness, 57—59 per cent of the hydrocyanic acid are obtained, which corresponds to the cyanogen of the cyanide of potassium. On distilling in a current of water-vapour, 86·49 per cent passed over; nearly the same amount (85·6 per cent) on twice distilling 3 parts of salt and 2 parts of sulphuric acid. If the distillation was repeated four times, the quantity of hydrocyanic acid obtained was more than corresponded to the cyanide of potassium; the residuary sediment amounted only to 21·16 per cent of the salt employed, and the filtrate contained a salt of sesquioxide of iron. Hence it is impossible to state how much per cent of the cyanogen in ferrocyanogen is obtained in the form of hydrocyanic acid, inasmuch as it depends altogether on the mode of distilling. The acid of the Pharmacopœia should be prepared with the aid of an analytical experiment.

(1) Arch. Pharm. [2] LV, 11.

Chloro-cyanide of hydrogen.

Chlorocyanide of Hydrogen.—On treating an aqueous solution of hydrocyanic acid with chlorine, and condensing the vapour disengaged in this reaction, after having passed through a chloride of calcium tube, by means of a frigorific mixture, Wurtz(1) obtained a liquid containing chlorocyanide of hydrogen, hydrochloric and hydrocyanic acids; by agitation with 2 or 3 vol. of water, the latter compounds were removed. By another rectification over chloride of calcium, the chlorocyanide of hydrogen is obtained in a state of purity; it is a colourless, mobile, very pungent liquid, causing violent lachrymation, which boils at 20° and burns with a violet flame; its aqueous solution yields a white precipitate with nitrate of silver. It contains $C_6 N_3 Cl_2 H$, whence it may be considered as a compound of hydrocyanic acid with the chloride of cyanogen $C_4 N_2 Cl_2$. With dry chlorine it yields hydrochloric acid and solid chloride of cyanogen $C_6 N_3 Cl_3$.

Liquid Chloride of Cyanogen.—Wurtz states farther, that chlorocyanide of hydrogen, when treated with protoxide of mercury (mixed with chloride of calcium and well cooled) and distilled after some hours in the water-bath, yields a colourless liquid, likewise powerfully attacking the eyes and the mucous membrane, which boils at 16° and solidifies at —7° to a crystalline mass. The vapour is not inflammable; the solution in water is not affected by nitrate of silver. Potassa gives rise to the formation of cyanic and hydrochloric acids, or rather of carbonic acid, ammonia, and chloride of potassium. The formula is $C_4 N_2 Cl_2$.

Cyanide of Potassium.—In the preparation of cyanide of potassium, a grey product is frequently obtained, if the mixture of ferrocyanide of potassium and carbonate of potassa be exposed to a bright red heat, until the mass is in a state of quiet fusion. This may be avoided, according to Clemm(2), by removing the crucible from the fire as soon as the dull-red-hot mass appears clear and a sample taken out is perfectly white; the evolution of gas having ceased, the deposition of the iron may be accelerated by gentle percussion, and the cyanide of potassium passed through a finely perforated hot iron spoon, and collected in a tall, smooth-walled vessel of silver, iron or porcelain, in which it is allowed to cool slowly. Grey cyanide of potassium may be added in new fusions, and treated by the above process, when it will become white.

Cyanate of Potassa.—Clemm(3) recommends for the preparation

(1) Compt. Rend. XXIV, 437; Ann. Ch. Pharm. LXIV, 367.
(2) Ann. Ch. Pharm. LXI, 250. (3) Ibid. LXVI, 382.

of cyanate of potassa, to fuse 8 parts of ferrocyanide of potassium and 3 parts of carbonate of potassa, and to introduce gradually into this mixture, somewhat cooled after fusion, but still liquid, 15 parts of minium, care being taken to avoid too considerable a rise of temperature. The crucible is now placed once more in the fire, and the mass well stirred, poured out and allowed to cool. If the salt is to be used for the preparation of urea, the mass is directly saturated with cold water and mixed with sulphate of ammonia (8 parts, if the above proportions have been employed), which may be dissolved in the washings. The mixture is evaporated and treated in the usual manner. If ferrocyanide of potassium should be present in the alcoholic solution, it may be separated by carefully adding sulphate of sesquioxide of iron, and pouring off the clear solution from the prussian blue which forms; 4 parts of anhydrous ferrocyanide of potassium yield 4—5 parts of urea. Cyanate of potassa.

Cyanide of Lead.—L. Kugler(1) has examined the yellowish-white precipitate, which, on addition of hydrocyanic acid and ammonia, is produced in a solution of basic acetate of lead, and which hitherto has been considered to be Pb Cy. He proposes the formula Pb Cy, Pb O, HO, which does not, however, agree with the results of his analysis. He found 87·22 per cent of lead, 5·07 of cyanogen, and 1·53—1·80 of water. If the water be considered as belonging to the compound, these numbers agree best with the formula 3 PbO, Pb Cy, HO, which requires 87·5 of lead, 5·4 of cyanogen, and 1·8 of water.

Double Compounds of Cyanide of Mercury. — H. Custer(2) has added some new members to the numerous class of double compounds of cyanide of mercury. They were obtained by dissolving the respective salts in proportions corresponding to the formulæ, and crystallizing. *Cyanide of mercury—iodide of sodium,* 2 Hg Cy, Na I + 4 HO forms four-sided satiny prisms, which lose the last portion of water only at 210°. They are easily soluble in water and in spirits of wine, and are decomposed by mineral acids into hydrocyanic acid and protiodide of mercury. *Cyanide of mercury—iodide of barium* 2 Hg Cy, Ba I + 4 HO, and *cyanide of mercury—iodide of strontium* 2 Hg Cy, Sr I + 6 HO, crystallize in square tables and exhibit a similar deportment. *Cyanide of mercury—bromide of calcium* 2 Hg Cy, Ca Br + 5 HO, is likewise soluble in water and in spirits of wine. A double salt of *cyanide of mercury* and *acetate of soda*

(1) Ann. Ch. Pharm. LXVI, 63.
(2) Arch. Pharm. [2] LVI, 1; Chem. Gaz. 1849, 101.

Double cyanides.

$Hg\ Cy + NaO, C_4 H_3 O_3 + 2\ HO$, was obtained once from the mother-liquor of the solution of the two salts.

Compounds with ammonia.

Double Cyanides. Compounds with Ammonia.—On mixing, according to Monthiers(1), an ammoniacal solution of a salt of protoxide of copper with ferrocyanide of potassium, a bright-yellow, crystalline powder is precipitated, which evolves ammonia only at a temperature of 130°, cyanide of ammonium being disengaged at a higher temperature. This compound is ferrocyanide of copper-ammonia $Cu_2\ Cfy + 2\ NH_3 + HO$ (Cfy = ferrocyanogen = $Fe\ Cy_3$). The same salt has been previously obtained by Bunsen(2), who found, however, only half the quantity of water. When moist, this substance (as does ferrocyanide of copper $Cu_2\ Cfy + 9\ HO$), absorbs, with evolution of heat 39·1 per cent of ammonia, a green compound $Cu_2\ Cfy + 4\ NH_3 + HO$ being formed, which loses part of the ammonia when exposed to air. Ferrocyanides of zinc and silver exhibit a similar deportment.

Subcyanide of Copper-Cyanide of Potassium.—Monthiers prepares this compound, which was discovered by Ittner, and more accurately examined by L. Gmelin and by Rammelsberg, by passing the vapour of hydrocyanic acid into potassa, containing hydrated protoxide of copper in suspension, until the latter is dissolved, a colourless liquid being produced. Monthiers confirms the formula $Cu_2\ Cy, K\ Cy$, established by Rammelsberg. By the action of potassa on fused subcyanide of copper, Rammelsberg(3) obtained a salt, of the formula $3\ Cu_2\ Cy, 2\ K\ Cy$.

Subcyanide of Copper-Cyanide of Ammonium.—Addition of sulphate of protoxide of copper to subcyanide of copper and cyanide of ammonium, produces a yellow precipitate, which turns green, cyanogen being evolved, and to which Monthiers assigns the formula, $NH_4\ Cu\ Cy, 2\ Cu_2\ Cy, HO$.

Ferrocyanide of Copper, Ferrocyanide of Copper and Potassium.—According to Rammelsberg(4), a solution of sulphate or acetate of protoxide of copper, when precipitated by hydroferrocyanic acid, yields pure ferrocyanide of copper, containing $Cu_2\ Cfy + 7\ HO$, when dried over sulphuric acid; according to Monthiers' statement, this salt contains 9 eq. of water. On pouring, drop by drop, a solution of a salt of protoxide of copper into an excess of ferrocyanide of potassium, Mosander obtained the anhydrous compound $Cu\ K\ Cfy$;

(1) J. Pharm. [3] XI, 249; J. Pr. Chem. XLI, 113; Ann. Ch. Pharm. LXIV, 297.
(2) Pogg. Ann. XXXIV, 134. (3) Ibid. LXXIII, 117.
(4) Ibid. LXXIV, 65.

according to Rammelsberg, it contains 2 eq. of water, and is expressed by the improbable formula, Cu_2 Cfy + K Cy, Fe Cy + 2 HO. On the other hand, if an excess of copper-salt be gradually mixed with ferrocyanide of potassium, a compound, Cu_2 Cfy, K_2 Cfy, 2 HO + 9 (Cu_2 Cfy + 7 HO) (?), is produced. Ferrocyanide of potassium.

Ferricyanide of Potassium.—For preparing ferricyanide of potassium, Rieckher(1) recommends to pass a slow current of chlorine through a dilute and cold solution of the yellow prussiate until it appears dark-red in transmitted light, when the liquid is rapidly evaporated to dryness. The residue is treated with 4 times its weight of water, and the filtrate boiled down to half its bulk.—Kolb(2) proposes to add, in small proportions, chlorate of potassa and hydrochloric acid to the boiling solution.

Ferricyanide of Potassium as an Oxidizing Agent.—The oxidizing power exerted by ferricyanide of potassium in the presence of potassa, as pointed out by Boudault(3), by which several heavy oxides are converted into higher oxides, and oxalic into carbonic acid, has been used by J. Mercer(4) in calico-printing (according to his statement previously to Boudault's communication), for discharging indigo. As a lecture-experiment, calico coloured with indigo may be moistened with ferrocyanide of potassium and afterwards immersed into a dilute solution of potassa. According to Monthiers(5) ferricyanide of potassium, when treated with ammonia, disengages nitrogen, ferrocyanides of potassium and of ammonium being formed.

Cobalticyanogen-Compounds.—C. Zwenger(6) has published a careful investigation of the cobalt-salts, corresponding to the ferricyanogen-compounds.—*Hydrocobalticyanic acid*, H_3 Co_2 Cy_6 + HO, is best prepared by decomposing cobalticyanide of copper, by means of hydrosulphuric acid, filtering and evaporating the colourless solution. It may be obtained, likewise, by decomposing with a slight excess of concentrated sulphuric, or nitric acid, a concentrated aqueous solution of cobalticyanide of potassium, adding absolute alcohol, and recrystallizing the residue which remains after the evaporation of the filtrate. This acid crystallizes in colourless, transparent, deliquescent needles, which possess a strongly acid taste.

(1) Jahrb. Pr. Pharm. XV, 1. (2) Ibid. XVI, 332.
(3) J. Pharm. [3] VII, 437; Berzelius' Jahresbericht, XXVI, 240.
(4) Phil. Mag. [3] XXXI, 126; Chem. Soc. Mem. III, 320; J. Pr. Chem. XLII, 43.
(5) J. Pharm. [3] XLII, 157; J. Pr. Chem. XLI, 118.
(6) Ann. Ch. Pharm. LXII, 157; J. Pr. Chem. XLIV, 173; J. Pharm. [3] XII, 380; Chem. Gaz. 1847, 417.

Cobalti-cyano-gen-com-pounds. It evolves carbonic acid from the carbonates, and dissolves iron and zinc, with disengagement of hydrogen; its aqueous solution is scarcely affected by ebullition. When heated beyond 100°, hydrocobalticyanic acid evolves water, then hydrocyanic acid, cyanide of ammonium, and carbonate of ammonia; at 250° a blue powder is formed, which at a still higher temperature, is decomposed into black carbide of cobalt. Hydrocobalticyanic acid is soluble in alcohol, but insoluble in anhydrous ether; it is not affected by hydrochloric acid, fuming nitric acid or aqua regia. When heated with concentrated sulphuric acid, it yields carbonic oxide, carbonic acid, sulphurous acid and sulphates of ammonia, and of protoxide of cobalt; if before complete decomposition, water be added, pale-red cobalticyanide of cobalt, $Co_3\,Co_2\,Cy_6 + 12\,HO$ is separated, which turns blue with loss of water. *Cobalticyanide of potassium*, $K_3\,Co_2\,Cy_6$, is formed, as indicated by its discoverer, L. Gmelin, by treating cyanide of cobalt with cyanide of potassium or carbonate of protoxide of cobalt with potassa and hydrocyanic acid, when hydrogen is evolved; if access of air be permitted, an absorption of oxygen takes place. In treating 100 parts of protocyanide of cobalt, $Co\,Cy, 2\,HO$ with cyanide of potassium, Zwenger obtained 0·65 of hydrogen; the decomposition, according to the equation $2\,Co\,Cy + 4\,K\,Cy + HO = K_3\,Co_2\,Cy_6 + KO + H$ requires 0·68.—From an aqueous solution of cobalticyanide of potassium, hydrocobalticyanic acid is precipitated by the addition of concentrated sulphuric and nitric acids. By boiling sulphuric acid the salt is decomposed like the acid. *Cobalticyanide of sodium*, $Na_3\,Co_2\,Cy_6 + 4\,HO$, is obtained like the two following salts; namely, by carefully neutralizing the acid with the carbonates. It crystallizes in long colourless needles, which are easily soluble, and lose their water (11·25 per cent) at 100°.—*Cobalticyanide of ammonium*, $(NH_4)_3\,Co_2\,Cy_6 + HO$, crystallizes in oblique four-sided plates, which are converted at 225° into cyanide of ammonium, carbonate of ammonia and a blue residue.—*Cobalticyanide of barium*, $Ba_3\,Co_2\,Cy_6 + 22\,HO$, forms easily soluble, colourless, transparent prisms, which lose 23·29 per cent = 16 eq. of water, at 100°.—*Cobalticyanide of copper*, $Cu_3\,Co_2\,Cy_6 + 7\,HO$, precipitated from a soluble salt of protoxide of copper by cobalticyanide of potassium or by hydrocobalticyanic acid, is of a light-blue colour; it loses, at 240°, 12·94 per cent (calculated 12·06) = 5 eqs. of water, and is decomposed by the fixed alkalies, with separation of protoxide of copper. Its solution in ammonia yields ultramarine-blue, brilliant, four-sided prisms, with eight-sided terminal pyramids, which are *ammonio-cobalticyanide of copper*, $Cu_3\,Co_2\,Cy_6 + 2\,NH_3 + 5\,HO$; they are

decomposed by acids into an ammonia-salt and cobalticyanide of copper, by alkalies, in the same manner as the latter compound.—*Cobalticyanide of cobalt*, $Co_3 Co_2 Cy_6 + 14 HO$, is obtained by precipitating salts of protoxide of cobalt with cobalticyanide of potassium, or with the acid itself, as a light-red powder, insoluble in water and acids, and losing the whole of its water at 220°, (calculated 29·25 per cent, found 28·93), becoming thereby intensely blue. It contains 2 eqs. of water more than the analogous compound produced by decomposition of the acid.—*Cobalticyanide of nickel*, $Ni_3 Co_2 Cy_6 + 12 HO$, can be obtained pure only by precipitating the solution of a salt of protoxide of nickel with an excess of hydrocobalticyanic acid; when freshly precipitated, it is gelatinous and light-blue; when dry it is of a greenish-blue colour, and has a conchoidal fracture. A solution of the freshly precipitated compound in ammonia, deposits, on evaporation or addition of alcohol, *ammonio-cobalticyanide of nickel*, $Ni_3 Co_2 Cy_6 + 2 NH_3 + 7 HO$, which is insoluble in water.—Carbonate of protoxide of lead is decomposed by hydrocobalticyanic acid, the solution deposits neutral *cobalticyanide of lead*, $Pb_3 Co_2 Cy_6 + 4 HO$, in small scales of nacreous lustre, which are insoluble in alcohol, and lose 3 eqs. of water at 100° and the fourth at 180°. Ammonia produces, in an aqueous solution of this compound, a white precipitate of basic cobalticyanide of lead, $Pb_3 Co_2 Cy_6 + 6 PbO + 3 HO$; the supernatant liquid contains only cobalticyanide of ammonium.—*Cobalticyanide of silver*, $Ag_3 Co_2 Cy_6$, is white, curdy, and insoluble in water and acids; its ammoniacal solution yields, on evaporation, colourless, transparent prisms of *ammonio-cobalticyanide of silver*, $Ag_3 Co_2 Cy_6 + NH_3 + HO$, which are insoluble in water, and part with ammonia and water only at 170°(1). Cobalticyanogen-compounds.

Platinocyanogen-compounds.—B. Quadrat(2) has described a series of platinocyanogen-compounds, the real existence of which has, however, to be decided by farther investigations.

Gmelin's cyanide of potassium and platinum, prepared by the ignition of spongy platinum with ferrocyanide of potassium, has been shown by the analyses of the discoverer and of Rammelsberg, which have likewise been confirmed by Quadrat, to possess the formula KCy, PtCy, in the anhydrous state. Knop obtained, by carefully treating a saturated solution of this salt with chlorine or nitro-

(1) It may here be stated, that cobalticyanide of potassium produces white precipitates with the nitrates of the oxides of mercury, but that it may be mixed with protochloride of mercury without being rendered turbid.

(2) Ann. Ch. Pharm. LXIII, 164; J. Pharm. [3] XII, 457.

Platino-cyanogen-compounds.

hydrochloric acid, the copper-red compound, $2\,KCy, Pt_2\,Cy_3$, containing sesquicyanide of platinum and potassium, which L. Gmelin (Handb. IV, 440) considers to be probably $K\,Cy, Pt\,Cy_2$.

According to Quadrat, if protochloride of platinum be added to an excess of cyanide of potassium, and the solution evaporated, long, thin, four-sided prismatic crystals are obtained, which appear yellow by transmitted, and bright-blue by reflected light. From the analysis of the anhydrous salt, Quadrat assigned to it the formula $Pt_5\,K_6\,Cy_{11} = 5\,(K\,Pt\,Cy_2) + K\,Cy$; when crystallized, it contains 21 eqs. (15·98 per cent) of water, of which 18 eqs. (14·03 per cent) are expelled at 100°. On boiling this salt with sulphuric acid, yellow protocyanide of platinum is precipitated, with which, by solution in cyanide of potassium, the original compound may be again prepared. It is soluble in 3 parts of water, and likewise in alcohol and ether; it gives a white precipitate with salts of protoxide of mercury, and a smalt-blue one with an excess of nitrate of suboxide of mercury. With sulphate of protoxide of copper, the light-green copper-compound, $5\,(Cu\,Pt\,Cy_2), Cu\,Cy$, insoluble in water and acids, is produced, which, by boiling with carbonate of soda, caustic baryta, strontia, or lime, furnishes the corresponding salts of these bases, $5\,(Na\,Pt\,Cy_2), Na\,Cy + 28\,HO$; $5\,(Ba\,Pt\,Cy_2), Ba\,Cy + 22\,HO$ and $5\,(Ca\,Pt\,Cy_2), Ca\,Cy + 27\,HO$; by decomposing the potassa-salt with sulphate of ammonia and the baryta-salt with sulphate of magnesia, the *platinocyanide of ammonium*, $5\,(NH_4\,Pt\,Cy_2), NH_4\,Cy$, and the *platinocyanide of magnesium*, $5\,(Mg, Pt\,Cy_2), Mg\,Cy + 19\,HO$, may be prepared. By digesting the copper-compound with ammonia and evaporating, blue needles were obtained, for which the approximate formula, $Cu\,Pt\,Cy_2, 2\,NH_3 + HO$, was arrived at. Hydrosulphuric acid decomposes platinocyanide of copper into protosulphide of copper, hydrocyanic acid and *hydroplatinocyanic acid*, $H\,Pt\,Cy_2$, which crystallizes in hydrated bluish-black or greenish-yellow crystals of golden lustre; it decomposes carbonates, yields, with ammoniacal gas, yellow platinocyanide of ammonium, and is split by sulphuric acid into protocyanide of platinum and hydrocyanic acid.

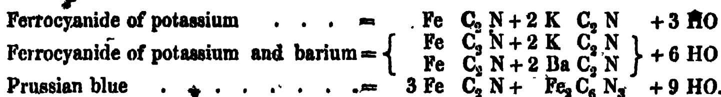
The same chemist(1) states, in a later communication, that the hydroplatinocyanic acid thus obtained, and likewise the salts prepared with it, contain a sulphocyanogen-compound; and that, by directly treating platinocyanide of copper (prepared from Gmelin's salt by sulphate of protoxide of copper) with calcined magnesia or with

(1) Ann. Ch. Pharm. LXV, 249.

baryta-water, platinocyanides of magnesium or barium are obtained, corresponding in composition to the potassium-compound. The analyses of these compounds, prepared by Baumert(1), according to the method described, confirm this statement. Quadrat found the mother-liquor, out of which the latter compounds had crystallized, to contain salts, differing in composition from the potassium-compound; they are colourless, and much more soluble in alcohol.—Laurent likewise considers Quadrat's salts to be analogous in composition to Gmelin's platinocyanide of potassium and the corresponding compounds; it may, however, from the preceding statements, be regarded as certain, that their preparation is attended by the formation of other compounds, which probably form double combinations with the true platinocyanides. Platino-cyanogen-compounds.

Cyanides of Platinum and Mercury and Nitrate of Suboxide of Mercury. —The formula of the smalt-blue precipitate, produced by nitrate of suboxide of mercury in cyanide of platinum and potassium, is, according to Rammelsberg(2), $Hg_2\,O, NO_5 + 5\,Hg\,Cy, Pt\,Cy + 10\,HO$; water resolves it into the two proximate constituents.—Quadrat considers the blue-salt prepared from his potassium-compound to be a combination of platinocyanide of mercury, $5\,(Hg\,Pt\,Cy_2)\,Hg\,Cy$, with variable quantities of nitrate of suboxide of mercury.

Cyanogen-compounds. Views respecting their Constitution.—Three views have as yet been taken of the ferrocyanogen compounds. According to the one:



Ferrocyanide of potassium . . . . =	$Fe\,C_2\,N + 2\,K\,C_2\,N + 3\,HO$
Ferrocyanide of potassium and barium =	$\left\{ \begin{array}{l} Fe\,C_2\,N + 2\,K\,C_2\,N \\ Fe\,C_2\,N + 2\,Ba\,C_2\,N \end{array} \right\} + 6\,HO$
Prussian blue . . . . =	$3\,Fe\,C_2\,N + Fe_2\,C_6\,N_3 + 9\,HO.$

The second view adopts as radicals, ferrocyanogen = $Fe\,C_6\,N_3$, ferricyanogen = $Fe_2\,C_{12}\,N_6$, platinocyanogen = $Pt\,C_4\,N_2$, platinicyanogen = $Pt_2\,C_{10}\,N_5$, &c. The third finally assumes a polymeric cyanogen, $C_2\,N$, $C_4\,N_2$, $C_6\,N_3$ . . . . $C_{12}\,N_6$ and so on, whose combinations, in Laurent's(3) opinion, may all be reduced to the formula $C_2\,N\,M$, (or $C_2\,N_2\,M_2$, according to Laurent and Gerhardt's equivalents), in which M may represent the sum of equivalents of two or three different metals. We here give an example of Laurent's formulæ, in which C6, = N=7, H=½, the equivalents of the metals being but half as high as those generally adopted, and in which, it must be borne

(1) Ann. Ch. Pharm. LXV, 250.
(2) Pogg. Ann. LXXIII, 117; J. Pr. Chem. XLI, 184; Berl. Acad. Ber. 1847, 115.
(3) Compt. Rend. XXVI, 294; J. Pr. Chem. XLII, 128.

Views respecting the constitution of cyanogen-compounds.

in mind, Laurent expresses protoxide of iron by $Fe_2 O$ (Fe_2=Fe according to the equivalent here adopted), sesquioxide of iron by $f_2 O$ ($f_2 = \frac{2}{3}$ Fe according to the usual equivalent,—the iron in the sesquioxide having only $\frac{2}{3}$ the equivalent of the iron contained in the protoxide), and that he assumes the equivalent of the platinum in the protoxide = $Pt_2 O$, as double that of the platinum in the binoxide = $pt_2 O$.

Ferrocyanides	$C_2 N_2 Fe_{\frac{2}{3}} M_{\frac{4}{3}}$.
Ferrocyanide of potassium . . .	$C_2 N_2 Fe_{\frac{2}{3}} K_{\frac{4}{3}} + HO$.
Ferrocyanide of potassium and barium .	$C_2 N_2 Fe_{\frac{2}{3}} Ba_{\frac{2}{3}} K_{\frac{2}{3}} + HO$.
Prussian blue	$C_2 N_2 Fe_{\frac{2}{3}} f_{\frac{4}{3}} + 2 HO$.
Ferricyanides	$C_2 N_2 f\ M$.
Cobaltocyanides	$C_2 N_2 Co\ M$.
Platinocyanides	$C_2 N_2 Pt\ M$.
Platini-platinocyanides . . .	$C_2 N_2 Pt_{\frac{2}{5}} Pt_{\frac{4}{5}} M_{\frac{4}{5}}$.

It is self evident that these are merely other expressions for known formulæ, and that they neither sustain nor found any new theory.

Comportment of Cyanogen-compounds at high Temperatures.—Rammelsberg(1) has investigated the behaviour of a series of cyanogen-compounds on exposure to high temperatures.

Protocyanide of silver is converted into paracyanide of silver, with disengagement, in the gaseous state, of half of the cyanogen, which does not possess, as stated by H. Thaulow, any properties differing from those of common cyanogen gas(2).—*Protocyanide of zinc* and *protocyanide of copper* likewise yield pure paracyanides; *protocyanide of nickel* and *protocyanide of cobalt*, on being heated, leave a black mass, which contains 12 equivalents of carbon and 1 of nitrogen to 6 equivalents of metal, and may be viewed as a paracyanide and carbide; *hydroferrocyanic acid* yields, first, water and hydrocyanic acid; the residuary protocyanide of iron likewise splits into paracyanide and carbide of iron, containing 20 equivalents of carbon and 5 of nitrogen to 12 equivalents of iron. *Ferrocyanide of potassium*, on being heated, leaves cyanide of potassium and carbide of iron, $Fe C_2$, as previously shown by Berzelius. *Ferrocyanide of calcium* and *ferrocyanide of zinc* exhibit the same comportment; *ferrocyanide of lead* disengages one-third of its carbon and one-half of its nitrogen, as

(1) Pogg. Ann. LXXIII, 80; Berl. Acad. Ber. 1847, 115; J. Pr. Chem. XLI, 180; Ann. Ch. Pharm. LXIV, 298.

(2) Comp. Liebig in Ann. Ch. Pharm. L, 357.

cyanogen- and nitrogen-gases; the residue consists of paracyanide of lead and paracyanide of iron, mixed with carbon. *Ferrocyanide of copper* yields, at 150^0, cyanogen-gas and a brownish-black mixture of paracyanides of copper and iron with carbon. Prussian blue (prepared from a salt of sesquioxide of iron and ferrocyanide of potassium, containing therefore a little potassium), which appears to contain, when dried in the air, 18 equivalents, and at 160^0 to 170^0, 9 equivalents of water, becoming anhydrous at 250^0, yields a residue amounting to about 60 per cent of the anhydrous substance which contains about 15 per cent of nitrogen, (3 equivalents of nitrogen and 7 equivalents of carbon to 7 equivalents of metal), and must hence be viewed as a mixture of paracyanide and carbide of iron. Comportment of cyanogen-compounds at high temperatures.

Cyanide of Mercury; Decomposition by Chlorine.—According to the investigations of Bouis(1), a hot saturated aqueous solution of protocyanide of mercury, treated with excess of chlorine, under the influence of solar radiation, is decomposed into protochloride of mercury, hydrochloric acid, and chloride of ammonium, which remain dissolved in water; into chloride of cyanogen, carbonic acid and nitrogen, which escape; and into a yellow oily fluid, amounting in quantity to one-fourth of the protocyanide of mercury, for which Bouis has proposed the formula, $C_{12}\,N_4\,Cl_{14} = C_8\,N_4\,Cl_8,\ C_4\,Cl_6$. It has a powerful odour, exciting to tears, a caustic taste, and is heavier than water, in which it is insoluble, but by which it is easily decomposed into hydrochloric and carbonic acids and nitrogen-gas(2). It is soluble in alcohol and ether, and becomes decolourized by keeping, sesquichloride of carbon, $C_4\,Cl_6$, being deposited. It explodes violently on being heated; by exposure only to a moderate heat, it is decomposed into nitrogen, some carbonic acid and a colourless liquid, which deposits, after a time, crystals of sesquichloride of carbon, $C_4\,Cl_6$; when pure, Bouis found this liquid to have the formula, $C_{20}\,N_4\,Cl_{22} = C_8\,N_4\,Cl_4 + 3\,C_4\,Cl_6$.

On gently heating the yellow compound, $C_{12}\,N_4\,Cl_{14}$ with strong nitric acid, a very powerful reaction ensues; nitrogen, carbonic acid, and nitrous fumes are evolved, and there are condensed in the receiver sesquichloride of carbon and a very volatile fluid, colourless when pure, and of a much more powerful odour than the preceding one; to the latter Bouis assigns the formula, $C_{12}\,N_4\,Cl_{14}\,O_4 = C_8\,N_4\,O_4\,Cl_8$,

(1) Ann. Ch. Phys. [3] XX, 446; J. Pr. Chem. XLII, 45; Ann. Ch. Pharm. LXIV, 305.

(2) A substance of very similar properties is produced by passing chlorine into a mixture of fulminate of protoxide of silver and water.

Cyanide of mercury; decomposition by chlorine.

$C_4 Cl_6$. It would, therefore, appear to be a simple product of oxidation of the first liquid.

The result of the action of ammonia on the yellow oil is the disengagement of gas, the formation of chloride of ammonium, of sesquichloride of carbon and of a red pulverulent substance, only slightly soluble in water, alcohol and ether, the nature of which has not yet been studied.—The yellow liquid detonates very violently with potassium.

The statement made by Aimé, and subsequently contradicted by Stenhouse, that a chlorocyanogen-combination of ethyl or methyl is produced by the action of chlorine on a solution of protocyanide of mercury in alcohol or pyroxylic spirit, has been likewise found incorrect by Bouis(1). He has shown the decomposition of the alcohol or hydrated oxide of methyl to be quite independent of the protocyanide of mercury, the cyanogen of which, in this reaction, is completely converted into carbonic acid, chloride of cyanogen, and chloride of ammonium.

Fulminic Acids. Their Constitution and Nomenclature.—The opinion of Berzelius(2), disputed by Liebig(3), that fulminic acid was a conjugate acid, in which a nitride, consisting of equal equivalents of both elements, was combined with the hypothetical acid, HO, $C_4 NO_3$, is considered by Fritzsche(4) to be a perfectly satisfactory expression of its constitution, receiving great support from the discovery of osman-osmic acid, whereby the existence of the questioned nitrides had been established beyond a doubt. He wishes to substitute for the names *silver-*, *mercury-*, *zinc-fulminic acid*, proposed in accordance with his view by Berzelius, the more rational ones *argentan-*, *mercuran-*, *cupran-*, and *zincan-tetranic acid*, constructed according to Berzelius's principle of nomenclature for products of dry distillation.—This view cannot easily be made accordant with the following facts.

J. H. Gladstone(5) has confirmed by analysis Liebig's statement(6) that urea and sulphocyanide of ammonium are formed in the decomposition of fulminate of protoxide of copper and ammonia

(1) Ann. Ch. Phys. [3] XXI, 111; J. Pr. Chem. XLII, 301; Ann. Ch. Pharm. LXIV, 316.

(2) Ann. Ch. Pharm. L, 426.

(3) Ibid. 429.

(4) Petersb. Acad. Bull. VII, 42; J. Pr. Chem. XLIV, 150.

(5) Chem. Soc. Qu. J. I, 228.

(6) Comp. Lancet, December, 1844.

by hydrosulphuric acid. He has submitted to analysis both products of decomposition, the urea as oxalate, the hydrosulphocyanic acid as sulphocyanide of silver. It is thereby shown that 1 eq. of fulminate of protoxide of copper and ammonia, and 3 eqs. of hydrosulphuric acid are decomposed into 1 eq. of protosulphide of copper, 1 eq. of urea, 1 eq. of hydrosulphocyanic acid, and 2 eqs. of water, Cyanuric acid.



$$CuO, N H_4 O, C_4 N_2 O_2 + 3 HS = CuS + C_2 N_2 H_4 O_2 + H C_2 N S_2 + 2 HO.$$

Cyanuric Acid.—If, according to de Vry(1), hydrochlorate of urea be heated to 145°, it splits into chloride of ammonium and pure cyanuric acid. At 320° the product of decomposition of urea, $C_6 N_4 H_4 O_4$, discovered by Liebig and Wöhler, is formed.—Wurtz(2) recommends the decomposition of fused urea by dry chlorine as the best method for the preparation of cyanuric acid. The products are cyanuric acid, chloride of ammonium, hydrochloric acid and nitrogen; the former substance is obtained by washing the mass with cold water.

According to Liebig, cyanuric acid is a tribasic acid $= 3\,HO, C_6 N_3 O_3$, in which all the hydrogen is contained in the form of replaceable water (witness the silver-salt). A closer investigation of its salts has led Wöhler(3) to consider this acid as bibasic $= 2\,HO, C_6 N_3 H O_4$, that is, as a conjugate cyanic acid, in which the urenic oxide of Berzelius, $C_2 N H O_2$,—isomeric with the hydrate of cyanic acid or with the insoluble cyanuric acid—is combined with 2 equivalents of cyanic acid.

Cyanurate of protoxide of silver, $2\,AgO, C_6 N_3 HO_4$, is prepared by dissolving carbonate of protoxide of silver in an excess of boiling cyanuric acid, or by dropping cyanurate of ammonia into an excess of a hot solution of nitrate of protoxide of silver, or, with greater certainty, by mixing hot solutions of cyanuric acid and acetate of protoxide of silver. It is a colourless crystalline powder, which is decomposed at 200°, but, in an atmosphere of hydrogen, is transformed even at 100° into the violet-black salt of the suboxide. It is insoluble in water and acetic acid, and easily decomposed by nitric acid. Digestion with concentrated ammonia converts it, without dissolution, into the salt, $2\,AgO, C_6 N_3 H O_4 + 2\,NH_3$, which loses

(1) Ann. Ch. Pharm. LXI, 249; J. Pr. Chem. XL, 498.
(2) Compt. Rend. XXIV, 436; Ann. Ch. Pharm. LXIV, 307.
(3) Ann. Ch. Pharm. LXII, 241; J. Pharm. [3] XII, 375. Laurent's Remarks, Ann. Ch. Phys. [3] XXIII, 114; J. Pr. Chem. XLV, 171.

Cyanuric acid.

the whole of its ammonia between 200° and 300°. Cyanurate of protoxide of silver is converted, by digestion with caustic potassa, into a compound in which, probably, one third of the base is potassa.

If, according to Liebig's directions for the preparation of tribasic cyanurate of protoxide of silver, excess of ammonia and then nitrate of protoxide of silver be added to a boiling solution of cyanuric acid, a salt separates in microscopic prisms, which evolves ammonia on treatment with potassa, and, when dried at 100°, loses the whole of its ammonia, yielding, on analysis, 70·55 per cent of silver; it contains hydrogen as an essential element, and has the formula, $3\ AgO,\ C_6\ N_3\ HO_4$.—The hot liquid decanted from this salt deposits, on cooling, a white compound, which, according to Wöhler, has probably the formula, $3\ AgO,\ C_6 N_3 HO_4 + 3\ NH_4\ O,\ C_6\ N_3\ HO_4$, (49·94 per cent of silver calculated, 49·4 per cent found), and which loses, at 250°, 2 equivalents of ammonia, and 1 equivalent of water. This substance is likewise formed, if nitrate of protoxide of silver, and crystallized cyanurate of ammonia, are mixed while hot, and the precipitate boiled with the liquid.—*Cyanurate of protoxide of lead*, $3\ PbO,\ C_6\ N_3\ H\ O_4 + 2\ HO$, is produced by adding freshly precipitated carbonate of protoxide of lead to an excess of hot cyanuric acid; by precipitating acetate of protoxide of lead with cyanurate of ammonia, or cyanuric acid; or, with greater certainty, by dropping basic acetate of protoxide of lead into an excess of a boiling solution of cyanuric acid. It forms microscopic prisms, with oblique terminal planes; when heated in an atmosphere of hydrogen, it is decomposed into cyanide of ammonium, urea, and metallic lead. By boiling it with nitrate of protoxide of silver, a salt of the formula $2\ Ag\ O,\ PbO,\ C_6\ N_3\ H\ O_4 + HO$, is produced.—*Copper-salts* of cyanuric acid could not be obtained of definite composition; on mixing dilute ammoniacal solutions of cyanuric acid and sulphate of protoxide of copper, a violet-blue salt, insoluble in water, is deposited, appearing under the microscope as amethyst-coloured four-sided prisms, with two broader lateral planes, and two-sided terminations, and having, probably, the composition, $2\ CuO,\ C_6\ N_3\ H\ O_4 + 2\ NH_3 + 3\ HO$.—If baryta-water be added, drop by drop, to a boiling solution of cyanuric acid, as long as the precipitate formed, redissolves, a crystalline *acid baryta-salt*, $2\ BaO,\ C_6\ N_3\ H\ O_4 + 2\ HO,\ C_6\ N_3\ H\ O_4 + 4\ HO$, is obtained, which loses 4 eqs. of water of crystallization at 280°. The *neutral baryta-salt*, $2\ BaO,\ C_3\ N_3\ HO_4 + 3\ HO$, is precipitated on addition of chloride of barium and

ammonia, or excess of baryta-water, to a hot solution of cyanuric acid.—Wöhler assigns to the difficultly soluble potassa-salt the formula, $2\,KO, C_6\,N_3\,H\,O_4 + 2\,HO, C_6\,N_3\,H\,O_4$, and to the salt which is decomposable by water, the formula, $2\,KO, C_6\,N_3\,H\,O_4$.—The investigations of Wurtz(1) are not in accordance with Wöhler's view of the constitution of cyanuric acid, inasmuch as he found the formula of cyanuric ether to be $3\,C_4\,H_5\,O + C_6\,N_3\,O_3$, and that of the corresponding methyl-compound, $3\,C_2\,H_3\,O, C_6\,N_3\,O_3$. Cyanuric acid.

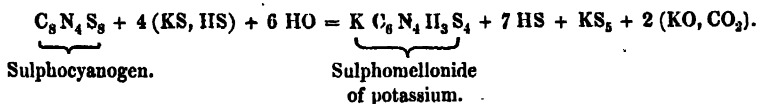
Sulphocyanide of Ammonium.—Liebig(2) has shown that cyanide of ammonium removes, from the higher sulphides of ammonium, the excess of sulphur which they contain beyond that in protosulphide of ammonium, forming with it sulphocyanide of ammonium, and has based upon this deportment a method for the preparation of the latter. The following proportions are advantageous: 2 parts of an aqueous solution of ammonia of the specific gravity 0·95, are saturated with hydrosulphuric acid, the resulting hydrosulphate of sulphide of ammonium is mixed with 6 parts of the same solution of ammonia, and to this mixture are added 2 parts of flowers of sulphur, and the distillate from 6 parts of ferrocyanide of potassium, 3 parts of sulphuric acid, and 18 parts of water. The mixture is digested in a water-bath, until the sulphur ceases to diminish in quantity, and the liquid has become yellow; it is then maintained in ebullition until the sulphide of ammonium is expelled, and the fluid has again become colourless. On filtering and evaporating to crystallization, 3¼ to 3½ parts of the dazzling white salt are obtained; ½ part of sulphur remains undissolved.

Mellon-compounds. Pseudo-sulphocyanogen and Hydrosulphomellonic Acid.—The so-called sulphocyanogen (prepared by the action of chlorine on sulphocyanide of potassium) was submitted to analysis by A. Jamieson(3), after having been treated with water until a salt of iron produced no colouration in the filtrate. (This treatment has to be continued several days, to ensure the removal of hydropersulphocyanic acid, which is very difficultly soluble in water, and the formation of which cannot be avoided in the preparation of the yellow substance). Jamieson arrived at the formula, $C_4\,N_2\,H\,S_4 + HO$, as expressing the composition of pseudo-sulphocyanogen, according to which it may be considered as a combination of equal equivalents of sulphocyanogen, hydrosulphocyanic acid, and water, $C_2NS_2 + HC_2NS_2 + HO$, or as 2 eqs. of hydrosulphocyanic acid, which have parted

(1) Compt. Rend. XXVI, 268.
(2) Ann. Ch. Pharm. LXI, 126. (3) Ibid. LIX, 339.

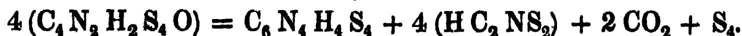
Pseudo-sulphocyanogen and hydro-sulpho-mellonic acid.

with 1 eq. of hydrogen, and assimilated 1 eq. of water(1). Pseudo-sulphocyanogen is converted, by treatment with hydrosulphate of sulphide of potassium, into sulphomellonide of potassium, sulphocyanide of potassium, pentasulphide of potassium, hydrosulphuric and carbonic acids. Jamieson constructs the following equation as explanatory of the formation of sulphomellonide of potassium, in which this body is supposed to be derived from the sulphocyanogen, which may be considered as combined in pseudo-sulphocyanogen with hydrosulphocyanic acid,



$$\underbrace{C_8 N_4 S_8}_{\text{Sulphocyanogen.}} + 4\,(KS, HS) + 6\,HO = \underbrace{K\,C_6 N_4 H_3 S_4}_{\text{Sulphomellonide of potassium.}} + 7\,HS + KS_5 + 2\,(KO, CO_2).$$

The following should have been appended to this equation, as explanatory of the decomposition of pseudo-sulphocyanogen (which Jamieson had not made his particular study): $C_8 N_4 H_4 S_8 + 4\,(KS, HS) = K_4 C_8 N_4 S_8 + 8\,HS$; according to his view, the formation of sulphocyanide of potassium required no particular explanation. Gerhardt and Laurent had adopted the formula, $C_6 N_3 H S_6$, for pseudo-sulphocyanogen, and hence explain(2) the formation of sulphomellonide of potassium by the following equation: $2\,(C_6 N_3 H S_6) + 4\,HO = C_6 N_4 H_4 S_4 + 2\,(H\,C_2 NS_2) + 2\,CO_2 + S_4$. Accordingly, they assume the pseudo-sulphocyanogen to be converted, in this decomposition, into hydrosulphomellonic acid, hydrosulphocyanic acid, carbonic acid, and sulphur. This is in accordance with Jamieson's view. It is singular, however, that Gerhardt and Laurent believe to have increased, by this equation, the probability of their formula for pseudo-sulphocyanogen, and consider it as a support of their view regarding the composition of this body. Jamieson's formula explains the decomposition in an equally simple manner:



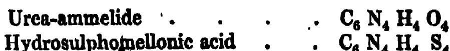
$$4\,(C_4 N_2 H_2 S_4 O) = C_6 N_4 H_4 S_4 + 4\,(H\,C_2 NS_2) + 2\,CO_2 + S_4.$$

According to Jamieson, one-half, according to Laurent and Gerhardt, only one-third of the carbon in the pseudo-sulphocyanogen is converted into hydrosulphocyanic acid; a determination of the hydrosulphocyanic acid, formed from a known amount of pseudo-sul-

(1) L. Gmelin's Remark (Handb. IV, 489) can only have reference to the amount of water in the pseudo-sulphocyanogen, and not to the composition of this substance, considered as anhydrous.

(2) J. Pharm. [3] XI, 228; Ann. Ch. Phys. [3] XX, 118.

phocyanogen, would decide which of the two formulæ is correct.— According to Gerhardt and Laurent, hydrosulphomellonic acid is urea-ammelide(1), in which the oxygen is replaced by sulphur:



Urea-ammelide	$C_6 N_4 H_4 O_4$
Hydrosulphomellonic acid . .	$C_6 N_4 H_4 S_4$

Mellonide of potassium.

Mellonide of Potassium.—Liebig(2) has described accurately the preparation of mellonide of potassium. Pure sulphocyanide of potassium is fused in a tubulated retort, the temperature is then raised, and crude mellon gradually introduced (about ¼ to ⅓ the weight of the sulphocyanide of potassium), whereby sulphur, ammoniacal products and bisulphide of carbon are volatilized. The mass, at first semi-fluid, is maintained in a state of gentle fusion, at a faint red heat, as long as any inflammable gas, emitting on combustion the odour of sulphurous acid, is evolved, and until the disengagement of cyanogen commences. If the operation has been successful, there are formed, during the cooling of the fused mass, while its temperature is still above the fusing-point of the sulphocyanide of potassium, stellated groups of thin needles; the absence of these shows that the temperature employed was not sufficiently high, or that the quantity of mellon added, was too small. The mass is treated with boiling water, filtered, and the filtrate allowed to cool, when a thick felt-like mass of white needles of hydrated mellonide of potassium is obtained, which may be freed from sulphocyanide of potassium by washing with alcohol, and recrystallization.

Kakodyl of Butyric Acid.—Wöhler(3) has shown, that by the dry distillation of equal parts of butyrate of potassa and arsenious acid, an oily colourless body is formed, which becomes orange-yellow, and then dark-brown, on exposure to air; it possesses a very nauseous kakodyl-like odour, and is not spontaneously inflammable in the air; it forms, with protochloride of mercury, an inodorous white compound. Wöhler has left it undecided, whether this body be a compound analogous to oxide of kakodyl, or whether it be that substance itself.

Acids and Collateral Matters. Mellitic Acid.—Erdmann and Marchand, and Schwarz, have published researches on mellitic

(1) Liebig and Wöhler in Ann. Ch. Pharm. LIV, 371.
(2) Ann. Ch. Pharm. LXI, 262; J. Pr. Chem. XL, 497.
(3) Ann. Ch. Pharm. LXVIII, 127.

Mellitic acid. acid.—The former chemists(1) always found mellitic acid, and its insoluble salts, prepared in the known manner from mellitate of ammonia, to be accompanied by an admixture of ammonia. In order to obtain the pure acid, they decomposed the ammonia-salt, by boiling it with excess of baryta, digested the baryta-salt with sulphuric acid, and purified the mellitic acid, thus obtained, from sulphuric acid, by recrystallization from water. The pure acid may be likewise obtained by decomposing with hydrosulphuric acid, the lead-salt, containing ammonia, precipitating the acid solution with acetate of protoxide of lead, washing the precipitate, decomposing it once more by hydrosulphuric acid, and repeating the process. The insoluble salts were prepared by precipitating the neutral solutions of the bases with the pure acid.—*Mellitate of protoxide of silver* retains a small amount of ammonia and water with great pertinacity; the crystalline, lustrous, scaly powder appears under the microscope as colourless, transparent, four-sided plates; it detonates on being heated, without development of electricity; the salt, dried in the air, gave on analysis less than 1 per cent of water; the formula, $AgO, C_4 O_3$, must be retained for it; the pure salt does not alter at 180°, but if it contains ammonia it blackens partially at this temperature, with formation of water.—*Mellitate of protoxide of lead,* $PbO, C_4 O_3$, likewise retains water obstinately (even at 180°).—*Mellitate of soda* crystallizes, on evaporation of cold saturated solutions, in large, irregular, striated crystals, belonging to an oblique-angular system, of the composition, $NaO, C_4 O_3 + 6 HO$ (the water escapes at 100°); from a warm concentrated solution it crystallizes in broad thin needles, $NaO, C_4 O_3 + 4 HO$ (nearly 3 eqs. of water escape at 100°, the whole at 180°).—*Neutral mellitate of potassa* forms easily efflorescent rhombic crystals being, according to Naumann, the combination, $\infty P . \infty \breve{P} \infty . 0P . \breve{P} \infty . \bar{P} \infty$; the following measurements were made, $\infty P : \infty P = 114°$, $\breve{P} \infty : 0P = 160°$, $\bar{P} \infty : 0P = 151°$; this salt has the formula, $KO, C_4 O_3 + 3 HO$, and is isomorphous with the ammonia-salt described by G. Rose(2). By addition of mellitic acid to a concentrated solution of the foregoing salt, the *sesquimellitate of potassa* is precipitated as a fine crystalline powder, which may be obtained, by recrystallization from water, in small nacreous plates, and has the formula, $2 KO, 3 C_4 O_3 + 9 HO$. —Erdmann and Marchand found *neutral mellitate of ammonia,*

(1) J. Pr. Chem. XLIII, 129; Ann. Ch. Pharm. LXVIII, 327, (in abstr.); J. Pharm. [3] XIV, 68.
(2) Pogg. Ann. VII, 336.

which precipitates as a fine powder on addition of a concentrated solution of ammonia to a solution of this salt, to be of the same composition as the crystals, to which this powder gradually changes, namely, $NH_4O, C_4O_3 + 3 HO$; the effloresced salt they found to contain 1 eq. less of water. On evaporating the solution, obtained by decomposing ammoniacal mellitate of protoxide of copper with hydrosulphuric acid, rhombic crystals of *trimellitate of ammonia*, $NH_4O, 3 C_4O_3 + 6 HO$, were obtained (according to Naumann's determination, $\infty P . \infty \bar{P} \infty . \infty \breve{P} \infty . 0P$; $\infty P : \infty P = 122^0$). On addition of mellitate of potassa to a neutral solution of a salt of protoxide of copper, a precipitate is formed, from which a portion only of potassa can be removed with great difficulty, by washing. On mixing acetate of protoxide of copper with mellitic acid in the cold, a light-blue gelatinous mass is formed, which becomes white by pressure, and blue and crystalline after dessication; if the jelly is allowed to stand, small crystalline nodules are formed, which increase to fine transparent dark-blue crystals; *mellitate of protoxide of copper*, thus prepared, is $2 CuO, 3 C_4O_3 + 12 HO$. If mellitic acid be added to a boiling solution of acetate of protoxide of copper, a flocculent precipitate is obtained; on washing, it loses a portion of its acid, becoming crystalline, and is represented, when dried in the air, by the formula, $CuO, C_4O_3 + 4 HO$. Ammoniacal mellitate of protoxide of copper forms beautiful azure-blue microscopic crystals, which, dried in the air, were found to have the composition $3 (CuO, C_4O_3) + NH_4O, C_4O_3 + 18 HO$ (at 120^0, 15 HO, and traces of ammonia escape).—The *mellitates of baryta* and *lime* appear to be anhydrous, but difficult of desiccation (compare the varying statements of Schwarz).—By prolonged ebullition of mellitic acid, containing still some sulphuric acid in admixture, with absolute alcohol, saturation of the liquid with baryta, removal of the excess of baryta, in the filtrate, by the carbonic acid of the atmosphere, and evaporation of the filtrate to dryness, over sulphuric acid, *in vacuo*, a gummy baryta-salt was obtained, the carbon of which was very difficult of combustion. This salt is, according to Erdmann and Marchand, *mellitate of oxide of ethyl* and *baryta*, $BaO, C_4H_5O, 2 C_4O_3$; it forms a clear solution with water; heated to 100^0 it undergoes partial decomposition, leaving, on subsequent treatment with water, carbonate of baryta. Mellitic acid.

Erdmann and Marchand state that they have also obtained the neutral mellitate of oxide of ethyl (mellitic ether), though not in a state sufficiently pure for analysis. Schwarz(1) was as unsuccessful

(1) Ann. Ch. Pharm. LXVI, 46.

Mellitic acid. in obtaining it as Wöhler. He likewise found that the insoluble salts of mellitic acid, when prepared by precipitating solutions of the metal with mellitate of ammonia, generally contained ammonia. According to him, mellitate of protoxide of silver is obtained pure by adding the solution of the ammonia-salt, drop by drop, to an excess of a boiling solution of nitrate of protoxide of silver; the silver-salt, thus prepared, remains white even at 200°, while the ammoniacal salt becomes violet-brown. Schwarz, also, confirmed the formula, $MeO, C_4 O_3$, for the salts of the protoxides of silver and lead, dried at 100°, and for the crystallized acid, $HO, C_4 O_3$; (after desiccation *in vacuo*, the latter only lost traces of moisture at 200°). *Mellitate of baryta*, prepared by double decomposition, separated as a thick gelatinous mass, becoming crystalline, and forming lustrous scales; he also obtained it, from very dilute solutions, in the form of fine needles; at 100° it only lost its hygroscopic moisture, retaining 1 eq. of water, which was expelled only at about 330°. The *mellitate of ammonia* was found, by Schwarz likewise, to have the formula, $NH_4 O, C_4 O_3 + 3 HO$, and the *mellitate of protoxide of copper*, $CuO, C_4 O_3 + 4 HO$ (3 eqs. of water escaped at 100°, the salt assuming a green colour, the fourth eq. was not perfectly expelled even at 230°).—Schwarz found *euchronic acid* to be best prepared by carefully heating mellitate of ammonia, over an open charcoal-fire, in a flat porcelain dish, stirring it continually, until the disengagement of ammonia ceases, and the salt is converted into a pale-yellow powder. He confirmed the formula, $2 HO, C_{12} N O_6$, for euchronic acid, dried at 200°; by adding baryta-water, drop by drop, in excess, to a solution of this acid, he obtained a pale-yellow pulverulent baryta-salt, corresponding closely in composition to $BaO, HO, C_{12} N O_6$.—He confirmed the composition of *paramide*, as being, $C_8 N H O_4$ (according to a later experiment of Wöhler, this substance, when boiled with acetate of protoxide of lead, is completely converted into mellitate of protoxide of lead, with formation of acetate of ammonia). When a solution of ammonia is poured on paramide, it immediately becomes yellow, voluminous, and is partially dissolved. If this solution be immediately poured into hydrochloric acid, a snow-white pulverulent substance precipitates, consisting of microscopic needles, somewhat soluble in water, which give with zinc the blue reaction of euchronic acid, and are re-precipitated from their ammoniacal solution by hydrochloric acid. If allowed to stand a day, the ammoniacal solution was found to contain only mellitate of ammonia. Schwarz considers the formula, $C_{\cdot 4} H_5 N_3 O_{14}$, as the most probable one for this substance, dried at 179° (when dried *in vacuo*, it contains 1 HO more); he calls it

Paramidic acid.—On submitting a solution of euchronic acid to the galvanic current, he observed that *euchrone* was deposited in small quantities at the platinum forming the negative pole. Oxalic acid.

Oxalic Acid.—L. Thompson(1) obtained, in eight experiments, from 28 ounces of cane-sugar, by treatment with 124 ounces of nitric acid, spec. grav. 1·245, in the first operation 17½ ounces; in the succeeding ones 30 to 32¼ ounces of crystallized oxalic acid, (the mother-liquor, containing oxalic acid, of the previous experiment being added in the next), and 20 to 22¼ of carbonic acid. He found the employment of concentrated nitric acid to produce too great a disengagement of heat, attended by the production of formic acid. He considers the final result of the reaction to be expressed by the following equation:

$$C_{12}H_{11}O_{11} + 7NO_5 = 6CO_2 + 2HO + 7NO_2 + 3(3HO, C_2O_3);$$

at the commencement of the process, the cane-sugar is converted into grape-sugar.

According to Anderson(2), hot aqueous solutions of equal equivalents of oxalic acid and chloride of potassium, chloride of sodium, or chloride of ammonium, yield, on cooling, quadroxalate of potassa, and binoxalate of soda, or of ammonia; the quantity of acid salt formed, varies according to the concentration of the fluid.

C. Schmidt has described the occurrence of oxalate of lime in the most simple cellular plants, and in the secretion of mucous membranes(3), as also the peculiar phenomenon of crystallization exhibited by this salt under the microscope(4).

Teroxide of bismuth, when boiled with binoxalate of potassa, was found by Schwarzenberg(5) to be converted into a white crystalline powder of *oxalate of teroxide of bismuth*, containing only traces of potassa, and having, when dried at 100°, the formula, $BiO_3, 3C_2O_3 + 4HO$.

Succinic Acid.—G. Reich(6) has pointed out the existence of succinic acid in nearly all the species of fossil woods, brown-coal, and pine-cones, found on the Baltic shores of the Samland.—Bley(7) recommends pharmaceutists to prepare their own succinic acid; he obtained (by employing glass retorts) from 16 ounces of amber, 0·4 to 0·85 ounces of succinic acid, 3 to 4½ ounces of oil, and 9 to 10½ ounces of colophony, (even on the addition of sulphuric acid, diluted

(1) Pharm. J. Trans. VIII, 117; Repert. Pharm. [3] I, 383.
(2) Chem. Soc. Qu. J. I, 231.
(3) Ann. Ch. Pharm. LXI, 288.
(4) Ibid. 307.
(5) Ann. Ch. Pharm. LXIV, 126.
(6) Arch. Pharm. [2] LIV, 155.
(7) Ibid LIII, 49.

Succinic acid.

with an equal weight of water, to the amber, this product was found to be applicable for varnish-making, after being washed with water containing soda). The distillation of 32 ounces of amber with 2 ounces of crude concentrated hydrochloric acid, yielded 1½ ounces of succinic acid, 21½ ounces of a greenish-brown tolerably liquid oil, and 3 ounces of nearly perfectly carbonized colophony.

Chlorosuccinic Acid.—Gerhardt(1) is of opinion that the true composition of chlorosuccinic acid (*acide chlorosuccique* of Malaguti(2), who assigns to it the formula $C_8 H_2 Cl_3 O_3$) is $C_6 H_3 Cl_3 O_4$, *i. e.* metacetonic acid, in which 3 H are replaced by 3 Cl.

Nicklès(3) has examined the crystalline form of chlorosuccinic acid; he, however, considers his measurements insufficient for the accurate determination of the axial system of this substance. It appears to crystallize in the monoclinometric system.

Malic Acid.—Dessaignes and Chautard(4) have made the observation that *neutral malate of lime*, left in contact with water for two days, was mostly converted into rough, transparent crystals, of about 1^{mm}. diameter; the composition of these crystals was found to be, $2\, CaO, C_8 H_4 O_8 + 6\, HO$; 5 eqs. of water are expelled at 100°. They did not succeed in a repetition of this metamorphosis. (These crystals are, however, always formed, if the juice of mountain-ash berries be nearly neutralized with milk of lime, and then be left undisturbed, instead of being boiled; when they are deposited generally after two or three days, often in thick crusts).

Nicklès has made angular measurements of the crystals of *bimalate of ammonia*. (Comp. p. 19).

Citric Acid.—Rogé-Delabarre(5) has recommended *citrate of magnesia* as a purgative, of agreeable taste; communications as to the best method of preparing this medicine, have been made by Mialhe(6), Massignon(7), and Winkler(8).

Action of Bromine on Citrates, Itaconates, and Citraconates.—Cahours(9) has studied the action of bromine on citrates, itaconates, and citraconates. On addition of bromine in small portions to a concentrated solution of citrate of potassa, the former disappears, heat and carbonic acid being disengaged. If bromine is

(1) J. Pharm. [3] XIV, 235. (2) Berzelius' Jahresbericht, XXVI, 772.
(3) Ann. Ch. Phys. [3] XXII, 31.
(4) J. Pharm. [3] XIII, 243; J. Pr. Chem. XLV, 48.
(5) J. Pharm. [3] XI, 431. (6) Ibid. XII, 27.
(7) Ibid. XII, 81. (8) Jahrb. Pr. Pharm. XVII, 280.
(9) Ann. Ch. Phys. [3] XIX, 484; J. Pr. Chem. XLI, 59; Ann. Ch. Pharm. LXIV, 350 (in abstr.); J. Pharm. [3] XIII, 292.

added until the effervescence ceases, and the fluid assumes a permanent reddish colour, and the excess of bromine be carefully removed by a dilute solution of potassa, an oily, colourless liquid, of aromatic odour, separates, which is a mixture of three different substances; the most volatile of these is bromoform (C_2 H Br_3; Cahours determined its spec. grav. as 2·90 at 12°, its boiling-point 152°, its vapour-density 8·63, by calculation 8·55, on the assumption of a condensation to 4 volumes); the least volatile product is crystallizable and partially decomposable by heat; the third substance is formed only in small quantity, and cannot be freed from the two former. If, in the distillation of the oleaginous fluid with water, the operation be interrupted as soon as oily drops cease to separate from the aqueous distillate, the residue in the retort solidifies, on cooling, to a crystalline mass; this being washed with water, and dissolved in boiling alcohol, the resulting solution, if saturated, deposits on cooling, long white needles, of silky lustre; if more dilute, broad transparent plates are obtained by spontaneous evaporation. The substance thus obtained, which is insoluble in cold and hot water, but soluble in alcohol, ether, and pyroxylic spirit, has the composition C_6 H Br_5 O_4, and is called by Cahours *bromoxaform*, it fuses at 74° to 75°; if the temperature is raised, it sublimes partially unchanged, the remainder is decomposed with liberation of bromine; it is dissolved by a concentrated solution of potassa in the cold, and decomposed by it under heat, with formation of bromide of potassium, oxalate of potassa, and bromoform; concentrated sulphuric acid dissolves it to a small extent at a gentle heat, and decomposes it, at the boiling temperature, with evolution of bromine and formation of an oily substance; moderately concentrated nitric acid has no action upon it in the cold, it dissolves a small portion by the aid of heat (depositing it again on cooling, in thin needles), while the remainder fuses to an oil, solidifying with crystalline texture, on cooling.—The citrates of soda and baryta comport themselves analogously to citrate of potassa; citrate of ammonia behaves differently; the action of bromine upon it causes an abundant evolution of carbonic acid, but no oleaginous fluid is formed.—The addition of bromine, drop by drop, to a concentrated solution of neutral itaconate or citraconate of potassa, produces an elevation of temperature, carbonic acid is evolved, and an oily liquid gradually separates. This is washed with potassa, upon which a slight residue, of an aromatic odour, remains behind; dilute hydrochloric acid separates from the alkaline solution, sometimes an oily, sometimes a butter-like substance, which soon solidifies; both bodies have the same composition, but differ, not only in their state

Action of bromine on citrates, itaconates, and citraconates.

Action of bromine on citrates, itaconates, and citraconates.

of aggregation, but also by the solid substance being more soluble than the liquid. The latter, when washed and dried *in vacuo* over sulphuric acid, is a pale amber-yellow liquid, possessing a peculiar odour, pungent taste, and a higher specific gravity than water; it is but slightly soluble in the latter, but dissolves in alcohol and ether in all proportions; its formula is $C_8\ H_6\ Br_2\ O_4$; when kept for a lengthened period, it sometimes remains liquid and sometimes crystallizes; it is partially decomposed on distillation, with evolution of hydrobromic acid and separation of carbon; it is scarcely attacked by moderately concentrated nitric acid, but is dissolved by concentrated sulphuric acid at a gentle heat, and partially reprecipitated by water; a concentrated solution of potassa decomposes it, with disengagement of heat and a very peculiar odour, so that an oily liquid is no longer separated from the alkaline solution by an acid; it is an acid substance (termed by Cahours, *Bromotriconic* acid), forming with ammonia a soluble salt, which crystallizes in yellowish-white scales, greasy to the touch, of the composition $N\ H_4\ O,\ 2\ (C_8\ H_5\ Br_2\ O_3)$; by decomposition of the ammonia-salt with nitrate of protoxide of silver, a silver-salt, $Ag\ O,\ C_8\ H_5\ Br_2\ O_3$, is obtained as a curdy precipitate, somewhat soluble in water, and becoming a tenacious mass after a little time; with oxide of ethyl it forms a liquid ether, $C_4\ H_5\ O,\ C_8\ H_5\ Br_2\ O_3$, which has a penetrating odour when heated; its flavour is similar to that of the radish, it is heavier than water, and undergoes partial decomposition by distillation. (It is prepared by dissolving the acid in alcohol, saturating with hydrochloric acid at 70^0 to 80^0, distilling and adding water to the distillate, upon which a heavy oil separates, which is washed first with alkaline and then with pure water). The solid acid, into which the liquid likewise occasionally changes, may be obtained by recrystallization from ether in the form of long needles, of silky lustre; it has the same composition as the foregoing liquid, fuses at a slightly elevated temperature, may be nearly completely volatilized by a gentle heat without decomposition, is tolerably soluble in cold and more so in boiling water, and separates from this solution, on cooling, in thin needles; it forms with the alkalies soluble and crystallizable salts; with the protoxides of lead and silver, slightly soluble compounds.—If bromine is allowed to act on a solution of citraconate of potassa, containing an excess of alkali, carbonic acid is likewise disengaged, and a yellowish oil formed, which is partially soluble in a dilute solution of potassa, an oil, of an agreeable odour, being left behind; the acid, taken up by the potassa, is separated from the alkaline solution, by acids, in white crystalline flakes, which are washed with a small quantity of water, pressed between

bibulous paper, and dried *in vacuo*. It is obtained, by recrystallization from ether, in the form of long needles, of the composition $C_6 H_4 Br_2 O_4$. This substance is tolerably soluble in cold, and more so in boiling water; it dissolves in all proportions in alcohol and in ether, and may be completely volatilized without decomposition by careful application of heat. Cahours has termed it ***bromitonic acid.*** —The acids, $C_8 H_6 Br_2 O_4$ and $C_6 H_4 Br_2 O_4$, may be regarded as butyric and metacetonic acids, in which 2 H are replaced by 2 Br. The compound, $C_8 H_6 Br_2 O_4$, could not be prepared by the action of bromine on butyric acid. By allowing the action of bromine on neutral citraconate of potassa to continue just until a few drops of the oily fluid had separated, Cahours obtained, by evaporation, a saline mass, partly soluble in alcohol; the addition of a few drops of sulphuric acid to the alcoholic liquid separated a substance soluble in water and in alcohol, of an odour similar to that of the volatile fatty acids, but less powerful, and rather different from that of butyric acid. By treating an alcoholic solution of $C_8 H_6 Br_2 O_4$ with potassium-amalgam, bromide of potassium was formed, and a potassa-salt remained dissolved in the alcohol, from which acids separated a crystallizable substance, very soluble, particularly so in hot water, and possessing the odour of the volatile fatty acids.—The aromatic liquid, mentioned several times previously, in the preparation of the brominated acids, as insoluble in dilute potassa, is likewise insoluble in pure water, but dissolves in alcohol and ether; it has a high specific gravity, and on being heated, evolves hydrobromic acid, leaving a carbonaceous residue. Its analyses correspond to the formula, $C_6 H_3 Br_3 O_2$, which Cahours, however, does not consider as definitively established.—The following is stated by Cahours respecting the action of bromine on salts of other organic acids. On adding bromine, drop by drop, to a slightly alkaline solution of oxalate of potassa or soda in the cold, no action ensues, but at a temperature of 40° to 50°, bromide of potassium or of sodium and carbonic acid are formed. Oxalate of protoxide of lead, or protoxide of silver, exhibit a similar behaviour. Bromine has no action on the acetates of potassa or soda. Alkaline pyromucates and pyromeconates are violently acted upon by bromine, with formation of a heavy reddish oil, and disengagement of fumes, of a penetrating odour, which strongly attack the eyes. Tartrate of potassa forms, with bromine, bromide of potassium and bitartrate of potassa; malate of potassa behaves with bromine like citrate of potassa, the products of decomposition do not, however, appear so marked. Alkaline tannates and gallates are violently acted upon by bromine; the only result, however, is a brownish resin, which is sometimes tenacious, sometimes brittle.

Action of bromine on citrates, itaconates, and citraconates.

Tartaric acid.

Tartaric Acid.—Mohr(1) has communicated some observations on the purification of *bitartrate of potassa* from the lime-salt; incidentally he has determined that 1 part of tartrate of lime is soluble in 6265 parts of water at 15°, and in 352 of boiling water. Knop(2) has found crude bitartrate of potassa to contain a yellow colouring matter, insoluble in carbonate of soda, but soluble in caustic ammonia or potassa.

The amount of water in several tartrates has been again determined by Berlin(3). He likewise found the crystallized *neutral potassa-salt* to contain $2\ KO,\ C_8\ H_4\ O_{10} + HO$, (the water is not expelled at 100°, but is so at 180°); *tartrate of potassa and soda* he found, like Schaffgotsch, Mitscherlich and Fresenius, to be $KO,\ NaO,\ C_8\ H_4\ O_{10} + 8\ HO$; the *tartrate of teroxide of antimony and potassa*, in whatever way it was prepared, had the formula $KO,\ SbO_3,\ C_8\ H_4\ O_{10} + HO$, (exposed to a stream of dry air at 100°, this salt rapidly loses about ⅔ of its water, the remainder escapes only very slowly; above 100°, the elements of water in the substance combine, and at 130° to 180°, one eq. of newly formed water escapes, at 200° to 220° a second is expelled); the *tartrate of teroxide of antimony and ammonia*, isomorphous with the former, is $NH_4\ O,\ SbO_3,\ C_8\ H_4\ O_{10} + HO$, (1 eq. of water escapes by the efflorescence of the salt, or more rapidly at 70° to 80°; at 100° 2 HO more are expelled; no ammonia escapes even at a temperature of 200°); the formula of a tartrate of teroxide of antimony and ammonia of an aqueous constitution different from the former, was found to be $NH_4\ O,\ SbO_3,\ C_8\ H_4\ O_{10} + 5\ HO$. This salt is deposited as a crystalline powder on rapidly cooling a solution of the double tartrate, and keeping it continually stirred, and sometimes also, alone or together with the former salt, on spontaneous evaporation of the solution, in large flat, easily efflorescing four-sided prisms, (the 5 eqs. of water of crystallization escape at 100°, together with 1 eq. of newly formed water); Berlin's formula for the *tartrate of teroxide of antimony and baryta* is $2\ (BaO,\ SbO_3,\ C_8\ H_4\ O_{10}) + 5\ HO$, in accordance with the determinations of Dumas and Piria, (at 100°, 2 eqs. of newly formed water escape, besides the 5 eqs. of water of crystallization; at 250° 2 farther eqs. are expelled); *tartrate of teroxide of antimony and protoxide of silver* was also found by him to be anhydrous.

(1) Arch. Pharm. [2] LIII, 161.
(2) Pharm. Centr. 1848, 63.
(3) Arch. Pharm. [2] LII, 257, (in abstr.); Ann. Ch. Pharm. LXIV, 358; J. Pharm. [3] XIV, 379.

According to F. Kessler(1), a mixture of a warm saturated solution of equal equivalents of tartrate of teroxide of antimony and potassa, and of nitrate of strontia, deposits a crystalline mass, which, by washing with hot water, dissolving in a cold solution of nitrate of strontia, and heating to 100°, may be obtained crystallized in small prisms. This compound is tartrate of *teroxide of antimony and strontia*, $SrO, SbO_3, C_8 H_4 O_{10}$; it may be heated to 210° for some time without sustaining any appreciable loss. By digesting it at 30° to 35° with a solution of 1 part of nitrate of strontia in 2 of water, and allowing the solution to evaporate spontaneously, fine large crystals of a compound $SrO, SbO_3, C_8 H_4 O_{10} + SrO, NO_5 + 12 HO$ are obtained which are easily soluble in cold water, (the foregoing salt separates from this solution on the application of heat). They are not affected by cold sulphuric acid, but are decomposed by warm acid with the formation, first of carbonic oxide, and then of binoxide of nitrogen and sulphurous acid. Tartaric acid.

Schwarzenberg(2) obtained, on boiling teroxide of bismuth with bitartrate of potassa, a clear syrupy filtrate, which was precipitated by acids, but not by water, and which yielded, by concentration in the water-bath, a heavy white crystalline powder of *tartrate of teroxide of bismuth and potassa*, having, when dried at 100°, the composition $KO, BiO_3, C_8 H_4 O_{10}$; it was decomposed by water, (the latter becoming acid, without containing any bismuth in solution).

Marsson(3) has contributed to our knowledge of the tartrates of sesquioxide of iron and potassa.—With respect to the compounds resulting from acid tartrate of potassa and boracic acid or biborate of soda, Krug(4) has endeavoured to establish the view that the boracic acid does not exist in them as a base (analogous to the teroxide of antimony in the tartrate of antimony and potassa), but that these substances contain a peculiar conjugate acid, consisting of boracic and tartaric acids.

Metamorphoses of Tartaric Acid by Heat.—Fremy(5) had stated, that crystallized tartaric acid ($2 HO, C_8 H_4 O_{10}$), lost by heating, first ½ HO, being converted into tartralic acid, that it then, by the loss, altogether, of 1 HO, changed into tartrelic acid, and that at last by losing 2 HO it became anhydrous tartaric acid. Laurent

(1) Chem. Gaz. 1849, 97; Pogg. Ann. LXXV, 410; J. Pr. Chem. XLV, 361, (in abstr.); Ann. Ch. Pharm. LXVIII, 334.
(2) Ann. Ch. Pharm. LXI, 244.
(3) Arch. Pharm. [2] LIII, 169.
(4) Arch. Pharm. [2] LV, 17.
(5) Ann. Ch. Phys. [2] LXVIII, 353.

Metamorphoses of tartaric acid by heat.

and Gerhardt(1) make the following statements: crystallized tartaric acid, when carefully heated in an oil-bath until just perfectly fused, is converted, without loss of weight, into another acid, *metatartaric acid*, which has the appearance of a transparent gum, is deliquescent, forms, with potassa and ammonia, acid salts of different forms of crystallization, and of greater solubility than the tartrates, does not precipitate lime-salts by itself, and only slowly and from concentrated solutions, when neutralized with ammonia, producing a precipitate, which is soluble in much water, and of a crystalline form, different from that of tartrate of lime. According to Pasteur's observation, it deflects the plane of polarization in the same direction as tartaric acid. The acid metatartrate of ammonia soon separates, on addition of a little ammonia to fused tartaric acid, in the form of groups of needles; its composition is the same as that of bitartrate of ammonia, (NH_4O, HO, $C_8H_4O_{10}$), it may be recrystallized from its solution in luke-warm water, but is converted, by boiling, into the tartrate. The acid metatartrate of potassa corresponds in appearance, behaviour, and composition to the former salt. If metatartaric acid be neutralized with potassa, alcohol precipitates a transparent oil which slowly solidifies to tartrate of potassa. The neutral lime-salt, when crystallized, is $2\,CaO$, $C_8H_4O_{10}+8\,HO$, dried at 160^0 it contains 2 eqs. of water, at 230^0 it becomes anhydrous. When once crystallized, it is difficultly soluble in boiling water, by which it is converted into common tartrate. The neutral baryta-salt precipitates on addition of a salt of baryta to neutral metatartrate of ammonia, in the form of a series of globules, having the same composition as the crystallized tartrate of baryta.—If tartaric acid be kept in fusion for a longer period, there is formed, besides the former acid, another, viz.: *isotartaric acid*, the neutral salts of which are isomeric with the acid tartrates, and whose lime-salt (a very soluble neutral, syrupy, uncrystallizable compound) becomes acid on boiling; this reaction is accompanied by the formation of metatartaric acid and neutral metatartrate of lime. This lime-salt, in an impure state, is Fremy's tartralate of lime. It is procured, not quite free from metatartrate of lime, by heating tartaric acid a little above its fusing point for some time, and saturating the aqueous solution of the mass with carbonate of lime, when, besides a tenacious insoluble salt (the so-called tartrelate), a very soluble neutral salt is obtained. It may be prepared pure from isotartridic acid formed by heating tartaric acid to

(1) Compt. Rend. XXVII, 318; Instit. 1848, 293; Laurent und Gerhardt's Compt. Rend. des Trav. Chim. 1848, 1 (J. Pr. Chem. XLVI, 360) and 97.

intumescence, as will be presently described; by dissolving this acid in cold water, saturating with ammonia, mixing the liquid with a concentrated solution of acetate of lime, and adding alcohol drop by drop, while the mixture is kept stirred, it separates as a thick, transparent oil, scarcely coloured; the supernatant liquid is poured off and alcohol added to the precipitate, which is still kept continually stirred, when the whole soon becomes solid and apparently crystalline; the mass is then washed with alcohol and dried. If the operation has been conducted rapidly, a neutral salt, easily soluble in cold water, is obtained, which, dried at 160°, has the composition CaO, C_8 H_5 O_{11}. Isotartrate of potassa precipitates as an oil, on adding isotartridic acid in the cold to a slight excess of an alcoholic solution of potassa; it is uncrystallizable and deliquescent, and is converted by heat into the acid metatartrate. The isotartrate of ammonia, obtained in the same manner, is likewise uncrystallizable and is converted by heat into the acid metatartrate, without loss of ammonia. When added to acetate or sulphate of protoxide of copper, it produces no precipitate, but, on addition of alcohol, the isotartrate of protoxide of copper separates as a glutinous green salt.—The tenacious lime-salt, discovered by Braconnot, which is obtained from tartaric acid, subjected to a higher temperature, and saturated with carbonate of lime, was considered by Fremy to be tartrelate of lime (comp. p. 390); according to Laurent and Gerhardt the acid contained therein is *isotartridic acid* (the hydrate, according to the generally adopted view), isomeric with anhydrous tartaric acid (C_8 H_4 O_{10}). The salts of isotartridic acid are easily prepared by the addition of the acid to solutions of acetates; with alkalies, however, it immediately forms isotartrates. Isotartridic acid renders lime-water turbid and produces a syrupy precipitate with acetate of lime or baryta, but not with nitrate of baryta. The lime-salt is prepared by a method similar to that for the isotartrate. The composition of the isotartridates of baryta, strontia and protoxide of lead was found to be expressed by the formula MO, C_8 H_3 O_9.

Metamorphoses of tartaric acid by heat.

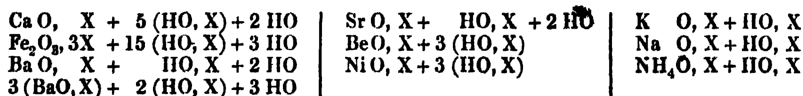
Pyrotartaric Acid.—Arppe(1) has accurately investigated pyrotartaric acid. He prepared it, according to the directions given by Millon and Reiset, by distilling pulverized tartaric acid with powdered pumice-stone (carbonic acid, water, some acetic acid and empyreumatic oil being produced, besides pyrotartaric acid). The aqueous was separated from the oily distillate by a wet filter, and

(1) In abstract from "Dissert. de Acido Pyrotartarico, Helsingf. 1847," in Ann. Ch. Pharm. LXVI, 73.

Pyrotartaric acid.

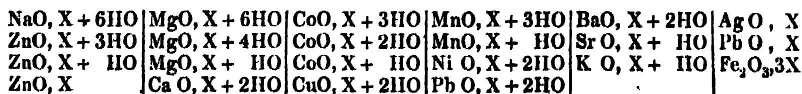
evaporated at a gentle heat, till it commenced to crystallize; the resulting crystalline mass was spread on bibulous paper, in an atmosphere of alcohol-vapour, by which means the impurities were dissolved and absorbed; the aqueous solution of the crystals thus purified was digested with nitric acid, crystallized, and the crystals fused, to expel the nitric acid; the pure pyrotartaric acid thus obtained, amounted to 7 per cent of the weight of tartaric acid employed.—Pyrotartaric acid has an agreeable and cooling acid taste, it is inodorous, fuses, and commences to vaporize at 100°, it boils at 190°, upon which the boiling-point gradually rises to 220°. It is soluble in 1½ parts of water, at about 20°, and expels carbonic acid from its combinations. Its composition, in the crystalline state, or fused at 100°, is, $HO, C_5 H_3 O_3$ (as already stated by Pelouze). After fusion and continued ebullition in a glass tube, it crystallizes no longer, or only partially; the portion that remains fluid has no acid reaction, and separates from water in the form of oily drops, which, however, disappear after some time. This oily fluid is obtained pure, by distilling pyrotartaric acid with anhydrous phosphoric acid (in the first portion of the distillate); it is colourless, inodorous at 20°, and smelling of acetic acid at 40°; it is heavier than water, remains fluid at 10°, and boils at 230° almost without decomposition; it is neutral, easily soluble in alcohol, and reprecipitated by water, and becomes converted by the latter, and even more rapidly by the alkalies, into crystallized pyrotartaric acid.—It has the composition of anhydrous pyrotartaric acid.—With respect to the formulæ of the pyrotartrates analysed by Arppe, he has given the following synopsis (X representing $C_5 H_3 O_3$):

ACID SALTS.



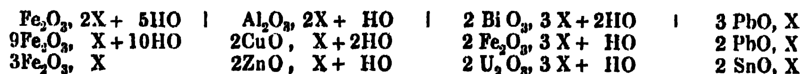
$CaO, X + 5(HO, X) + 2HO$	$SrO, X + HO, X + 2HO$	$K O, X + HO, X$
$Fe_2O_3, 3X + 15(HO, X) + 3HO$	$BeO, X + 3(HO, X)$	$Na O, X + HO, X$
$BaO, X + HO, X + 2HO$	$NiO, X + 3(HO, X)$	$NH_4O, X + HO, X$
$3(BaO, X) + 2(HO, X) + 3HO$		

NEUTRAL SALTS.



$NaO, X + 6HO$	$MgO, X + 6HO$	$CoO, X + 3HO$	$MnO, X + 3HO$	$BaO, X + 2HO$	AgO, X
$ZnO, X + 3HO$	$MgO, X + 4HO$	$CoO, X + 2HO$	$MnO, X + HO$	$SrO, X + HO$	PbO, X
$ZnO, X + HO$	$MgO, X + HO$	$CoO, X + HO$	$NiO, X + 2HO$	$K O, X + HO$	$Fe_2O_3, 3X$
ZnO, X	$CaO, X + 2HO$	$CuO, X + 2HO$	$PbO, X + 2HO$		

BASIC SALTS.



$Fe_2O_3, 2X + 5HO$	$Al_2O_3, 2X + HO$	$2 BiO_3, 3X + 2HO$	$3 PbO, X$
$9Fe_2O_3, X + 10HO$	$2CuO, X + 2HO$	$2 Fe_2O_3, 3X + HO$	$2 PbO, X$
$3Fe_2O_3, X$	$2ZnO, X + HO$	$2 U_2O_3, 3X + HO$	$2 SnO, X$

Racemic Acid.—Respecting Pasteur's statements on the composition of racemic acid, compare page 22. Laurent and Gerhardt

(in their researches, page 390) found that racemic acid could be likewise fused and converted into metatartaric acid, without loss of weight. Racemic acid.

Lactic Acid.—On the occurrence of lactic acid in flesh, *see* "Flesh."

On Bensch's prescription for the production of lactic acid, *see* "Butyric Acid."—Engelhardt and Maddrell(1) obtained, according to that prescription, from 18 pounds of cane-sugar, about 21 pounds of lactate of lime; the acid, separated from the salt of protoxide of zinc by hydrosulphuric acid, or from the lime-salt, by an exact equivalent of sulphuric acid, and evaporated to syrupy consistency, was further purified by solution in ether, and evaporation. With respect to the formation of butyric acid, they differ from Wackenroder's(2) opinion that this acid was not produced when a ferment free from fat was employed. They found that by using casein, free from fat, as a ferment with pure lactate of lime, and observing the other conditions requisite for the production of butyric acid, the conversion was readily effected, whereas, without the addition of a ferment, the pure lactate of lime remained unchanged. Access of air was found to accelerate the conversion of lactate of lime into butyrate, but not to be actually indispensable in the process. The gas generated during this change was found to consist of about 3 carbonic acid to 4 hydrogen. Engelhardt and Maddrell did not observe the formation of mannite, in the preparation of lactic acid from sugar, (which has been since shown to be always present, compare page 355), but noticed the production of a gummy substance. The syrupy mass, obtained by evaporation of the mother-liquor, was dissolved in boiling spirits of wine; from this solution separated, on cooling, a crystalline lime-compound, which, after recrystallization from alcohol, was found to have the composition, $CaO, C_{20} H_{14} O_{14} + 12 HO$ (the water escapes by exposure *in vacuo*); on precipitating the aqueous solution of this compound by carbonate of ammonia, and evaporating considerably, the syrup obtained had not the slightest sweet taste.—They, likewise, failed in obtaining lactic acid in the solid form, even at from -20^0 to -24^0.—The lactates investigated by them were found to be insoluble in ether, and difficultly soluble in cold water and alcohol; only a few of them were easily and considerably soluble in

(1) Ann. Ch. Pharm. LXIII, 83; J. Pr. Chem. XLIII, 390 (in abstr.); J. Pharm. [3] XII, 447 (in which Gerhardt claims the priority of considering lactic acid as bibasic).
(2) Arch. Pharm. [2] XLVII, 249.

Lactic acid. boiling alcohol, they are soluble to a greater extent in boiling water. All lactates, with exception of the salt of protoxide of nickel, part with the whole of their water of crystallization at 100^0; most of them may be heated up to from 150^0 to 170^0, and the lactate of protoxide of zinc up to 210^0, without decomposition.—If excess of carbonate of protoxide of silver be boiled with lactic acid, *lactate of protoxide of silver* crystallizes from the neutral solution formed, in silky needles, generally grouped in warty concretions, which easily blacken on exposure to light, and fuse, with decomposition, at 100^0; when dried in the air this salt is $AgO, C_6 H_5 O_5 + 2 HO$. It parts with its water at 80^0, and *in vacuo*.—*Lactate of protoxide of copper*, obtained in the same manner, and purified, by recrystallization, from a basic salt, which generally is produced simultaneously, forms large crystals, varying in colour between blue and green, which, according to Ettling's determination, are monoclinometric, and have the formula, $CuO, C_6 H_5 O_5 + 2 HO$; they are soluble in 115 parts of cold, and 26 parts of boiling water, the solution having a strongly acid reaction; by the addition of a little alcohol to the aqueous solution, the salt is obtained of a light-blue colour, and of satiny lustre, but of unaltered composition.—In the preparation of the preceding salt, soon after the solution has cooled, a basic salt is deposited, of a light-blue colour, and of the formula, $2 CuO, C_6 H_5 O_5$, when dried at 100^0; it is difficultly soluble in cold as well as boiling water, and may be separated, by levigation, as the heavier substance, from another basic salt, which is formed at the same time.—*Lactate of protoxide of cadmium* (prepared like the silver-salt) crystallizes from the solution, evaporated to the formation of a pellicle, in small, anhydrous, colourless needles, $CdO, C_6 H_5 O_5$; it is insoluble in cold and warm alcohol, but soluble in 10 parts of cold, and 8 of boiling water; the solution is neutral.—*Lactate of suboxide of mercury* is obtained by mixing concentrated solutions of lactate of soda, and of nitrate of suboxide of mercury. The mixture is at first colourless, but assumes afterwards a beautiful rose, or carmine colour; some mercury is deposited, and in about twenty-four hours magnificent groups of crystals, of the same colour, separate from the filtrate, in the form of rosettes. The formula of this salt is $Hg_2 O, C_6 H_5 O_5 + 2 HO$; at 100^0 it darkens, without being decomposed; it is difficultly soluble in water, cold or boiling, likewise in boiling alcohol, and is insoluble in cold alcohol. The solution has a strong acid reaction; the aqueous solution is decomposed by boiling, with separation of metallic mercury, and formation of a salt of the protoxide.—*Basic lactate of protoxide of mercury*,

$2\,HgO, C_6H_5O_5$, is produced by boiling protoxide of mercury with lactic acid till the solution is saturated, evaporating it to the consistency of syrup, and treating the crystalline mass, that separates, with boiling water, in which it dissolves, (leaving a light-yellow pulverulent residue); it crystallizes from this solution in highly lustrous, anhydrous prisms, easily soluble in cold and boiling water, but difficultly so in cold and boiling alcohol. The solutions have a strongly acid reaction, and are not decomposed by boiling.—*Basic lactate of protoxide of tin*, $2\,SnO, C_6H_5O_5$, separates as an anhydrous crystalline powder, on mixing lactate of soda with an acid solution of protochloride of tin; this powder is insoluble in cold and boiling alcohol, and in cold water, very slightly soluble in boiling water (yielding an acid solution), it dissolves freely in hydrochloric acid, and but slowly in acetic acid.—Addition of bichloride of tin to lactate of soda produces no precipitation, nor does the mixture, evaporated to syrupy consistency, deposit any crystals.—*Lactate of protoxide of lead* could not be obtained in the crystalline state, nor of definite properties; the neutral solution yields, on evaporation, a gummy mass, which is easily soluble in dilute spirit, but slightly so in alcohol, with application of heat.—*Lactate of sesquioxide of uranium* was formed by dissolving the sesquioxide in lactic acid, and evaporating to the consistency of syrup, when, on cooling, the anhydrous salt was deposited in light-yellow crusts ($U_2O_3, C_6H_5O_5$). It is but very little soluble in alcohol, but easily so in cold and boiling water. The solution has a strongly acid reaction, and is decomposed by solar radiation, with green coloration, and subsequent deposition of brown sesquioxide of uranium.—Teroxide of antimony is scarcely soluble in lactic acid, but dissolves to a considerable extent in acid lactate of potassa, no crystalline compound could, however, be obtained; nor could the combinations of lactic acid with the sesquioxides of iron and chromium, or with alumina, be obtained crystalline.—*Lactate of protoxide of iron* was prepared according to Pagenstecher's prescription (this salt separates after twenty-four hours from the mixture of lactate of ammonia with protochloride of iron), or better, by decomposing sulphate of protoxide of iron with lactate of baryta in a flask, at the boiling temperature, and adding alcohol to the filtrate; it crystallizes from water in tolerably large, pale-yellow needles, and from dilute spirit in small white needles; when dried in the air it has the composition, $FeO, C_6H_5O_5 + 3\,HO$; when exposed to the air it becomes oxidized, assuming a dark colour, and loses water at 50° to 60°. It is difficultly soluble in cold, and tolerably so in boiling water and

Lactic acid.

Lactic acid. alcohol, the solutions have an acid reaction, and become dark-brown on exposure to the air.—The formula of *lactate of protoxide of zinc*, in the crystallized state, and dried in the air, has been confirmed by Engelhardt and Maddrell as being, $ZnO, C_6 H_5 O_5 + 3 HO$; it dissolves, according to them, in 58 parts of cold, and 8 of boiling water, but is scarcely at all soluble in cold or in boiling alcohol; the solutions are acid. With the composition of this salt corresponds exactly that of the *lactate of protoxide of nickel* (which occurs in apple green needles, or crystalline crusts; losing 2 eqs. of water at 100^0, and the third only at 130^0); as does likewise that of the peach-blossom *lactate of protoxide of cobalt*, that of *lactate of protoxide of manganese* (which forms colourless, or pale-amethyst crystals), and that of *lactate of magnesia* (forming crystalline crusts, which are not efflorescent).—*Neutral lactate of lime* crystallizes from its concentrated aqueous solution in hard grains, consisting of concentric rings of radiating crystals, of the formula, $CaO, C_6 H_5 O_5 + 5 HO$ (Engelhardt and Maddrell found that the whole of the water was expelled at 100^0); they are soluble in 9·5 of cold water, and in all proportions in boiling water, but not at all in absolute alcohol; the aqueous solution is neutral. Lactate of lime is deposited from its solution, in dilute spirit, as a magma of crystals, which contain the same quantity of water as above-stated. The aqueous solution of this salt, mixed with excess of chloride of calcium, and concentrated considerably, produces prismatic crystals, not affected by the air, of the composition $CaCl + CaO, C_6 H_5 O_5 + 6 HO$, which are easily soluble in water and boiling dilute spirit, only slightly so in cold alcohol, but tolerably soluble in hot alcohol, and lose 5 HO at 110^0. By recrystallization of these crystals from water, a salt is obtained, containing a smaller amount of chlorine.—*Acid lactate of lime* is produced by adding lactic acid to a solution of the neutral lactate; crystals of the latter salt are first deposited from the solution, on concentration to syrupy consistency; nodules of radiated fibrous crystals are obtained, having the composition, $CaO, C_6 H_5 O_5 + HO, C_6 H_5 O_5 + 2 HO$. This acid salt is soluble in alcohol, loses 2 HO at 80^0, and is decomposed by exposure to a higher temperature.—*Lactate of strontia* is a neutral salt, similar to the lime-salt; when dried in the air it has the formula, $SrO, C_6 H_5 O_5 + 3 HO$, becoming anhydrous at 100^0.—*Neutral lactate of baryta* could not be obtained crystallized; the *acid lactate*, however, was produced as a distinctly crystalline salt of strongly acid reaction, unaffected by the air, and having, when dried in the atmosphere, the composition, $BaO, C_6 H_5 O_5 + HO, C_6 H_5 O_5$; at 100^0 it shrinks a little, and has an empyreu-

matic odour.—The potassa-, soda-, and ammonia-salts could not be obtained in crystals. Engelhardt and Maddrell believe lactic acid to be bibasic, and that its formula should be doubled, and are of opinion that the existence of the acid salts just described, and the conversion into butyric acid, are arguments in favour of this view(1). Lactic acid.

Engelhardt(2) has likewise investigated *lactate of teroxide of bismuth.* Carbonate, or hydrate of teroxide of bismuth, dissolves only to a small extent in lactic acid, without forming an insoluble salt; the strongly acid solution, after concentration, deposits, on cooling, small needles of a salt, which may be obtained in larger quantity by mixing excess of lactate of potassa, in the cold, with a solution of teroxide of bismuth in nitric acid, and dissolving, in as little water as possible, the magma of crystals which separates from concentrated solutions; lactate of teroxide of bismuth soon separates in crystalline crusts (a larger quantity is deposited, after a time, from the mother-liquor, on mixing it with spirit till it becomes milky); this salt is, $BiO_3, 2\,C_6\,H_5\,O_5$; it is only slightly soluble in cold, but more so in hot water; its solution in the latter does not, however, yield any crystals on cooling, but deposits the salt, upon concentration, in crystalline crusts, soluble in a small quantity of water, the solution being rendered very turbid by farther dilution.—On mixing hot solutions of lactate of soda, and nitrate of teroxide of bismuth, or upon adding the latter to excess of a moderately dilute solution of the former salt, and boiling, an abundant pulverulent precipitate of $BiO_3, C_6\,H_5\,O_5$ is formed, which is not dissolved or decomposed by boiling water.

Liebig(3) has observed that the lactic acid prepared from muscular flesh, forms a crystalline lime-salt, containing 4 eqs. of water, and a salt of protoxide of zinc, containing 2 eqs. He considered it possible, that this difference in the amount of water, from that hitherto found in these salts, might arise from his having produced the crystallized salts by evaporation, and not by cooling.—Engelhardt(4) has shown, however, that lactic acid (*a*) obtained from flesh, and that (*b*) prepared from sugar, really produce salts of different aqueous constitution; they differ, likewise, not only with respect to the temperature at which they part with their water, or

(1) It may be added that, in that case, the formula of lactic acid would stand in a more simple relation to that of milk-sugar, and of grape-sugar.

(2) Ann. Ch. Pharm. LXV, 367. (3) Ibid. LXII, 326.

(4) Ibid. LXV, 359.

Lactic acid. undergo decomposition, but also as to their solubility and external properties. The *a* lactate of lime, when crystallized from water, contains always 4, and the *b* lactate 5 eqs. of water; both crystallize from alcohol with 5 eqs. of water, but on recrystallizing the *a* lactate from water, it will again be found to contain 4 eqs. The *a* lactate of lime must be kept longer at 100°, than the *b* lactate, to lose all its water; the former requires 12·4, the latter 9·5 parts of cold water for solution. The *a* lactate of magnesia dissolves more easily in water and alcohol than the *b* lactate. The former most likely contains 4, the latter 3 eqs. of water. The *a* lactate of protoxide of zinc always contains 2, the *b* lactate 3 eqs. of water; the former parts with it slowly at 100°, and decomposes at 150°, while the latter loses its water rapidly at 100°, and shows, even at 210°, no signs of decomposition; the former is soluble in 5·7 of cold, and 2·88 parts of boiling water, in 2·23 parts of cold, and in almost the same quantity of boiling alcohol; the latter requires for solution 58 parts of cold, and 6 of boiling water, and is scarcely at all soluble in alcohol. The *a* lactate of protoxide of copper crystallizes in faint azure-blue wart-like concretions, the *b* lactate, in tolerably large brilliant, well-formed, dark-blue, or greenish crystals; the former dissolves in 1·95 parts of cold, 1·24 of boiling water, and much more easily in alcohol; the latter is soluble in 6 parts of cold, and 2·2 of boiling water, and in 115 parts of cold, and 26 of boiling alcohol; the *a* lactate loses but little water over sulphuric acid, and is, after lengthened exposure to 140°, only partially soluble in water, leaving a residue of suboxide of copper; while the water in the *b* lactate escapes rapidly over sulphuric acid, or at 100°, and the salt decomposes at from 200° to 210°, smouldering away, and leaving metallic copper. The former contains about 9 per cent of water, the latter 2 eqs. (18·0 per cent).—Liebig had obtained a basic salt of protoxide of zinc, with lactic acid from *Sauerkraut;* Engelhardt did not succeed in forming such a salt with the lactic acid from sugar. He considered it possible that *a* lactic acid may be monobasic (in combination with bases, $C_6H_5O_5$), and *b* lactic acid bibasic ($C_{12}H_{10}O_{10}$).—Heintz(1) has confirmed Engelhardt's observation with respect to the salt of protoxide of zinc, and has shown at the same time, that the *a* and *b* lactic acids differ in other respects than by the one containing less oxygen and hydrogen (in the same proportion as in water) than the other, and that it is only a retention of water by the

(1) Pogg. Ann. LXXV, 391; Chem. Gaz. 1849, 89.

salts of the former acid, which makes it appear isomeric with the latter; he proposes the name *paralactic acid* for that contained in muscular flesh. Igasuric acid.

Igasuric Acid.—Marsson(1) has again called attention to igasuric acid, discovered by Pelletier and Caventou in Ignatius-beans and *nux vomica*, which was found by Carriol to resemble lactic acid, and considered by Berzelius as identical with it. Marsson added to the liquid, from which strychnine and brucine had been separated by magnesia, acetate of protoxide of lead, when a copious precipitate was formed, (while lactate of protoxide of lead is easily soluble). Neither the liquid, obtained after decomposition of the lead-compound by hydrosulphuric acid, nor the compounds of the acid with lime, ammonia, or protoxide of zinc, could be made to crystallize. By saturation of the acid with baryta-water and removal of the excess of baryta with carbonic acid, an uncrystallizable salt was obtained, which, when dried at 100°, yielded on analysis an amount of baryta corresponding closely to that in lactate of baryta. Want of material prevented Marsson from making a more complete investigation.

Mucic Acid.—Hagen(2) has investigated mucic acid and its salts. He found the formation of mucic acid, by the action of nitric acid on milk-sugar, to be accompanied by the production of oxalic acid, and observed that the latter acid appeared to be formed principally as a direct product of oxidation of the milk-sugar and only in small quantity as a product of the oxidation of mucic acid; he also found that moderately concentrated nitric acid produced the largest quantity of mucic acid, and that, by employing concentrated nitric acid, probably a portion of the mucic acid was transformed into oxalic acid, while too dilute an acid converted the milk-sugar nearly exclusively into oxalic acid. In the most successful experiment he obtained from 100 parts of milk-sugar 35·9 of mucic acid(3).—Hagen agrees with the view that mucic acid is bibasic ($C_{12}H_8O_{14}$), and considers this view supported by the circumstance that, if the equivalent of the acid were halved, the amount of water contained in several mucates would stand in very complex and unusual atomic

(1) Arch. Pharm. [2] LV, 295.

(2) Pogg. Ann. LXXI, 531; Ann. Ch. Pharm. LXIV, 347 (in abstr.); J. Pharm. [3] XII, 310.

(3) Guckelberger obtained 60 to 65 per cent of mucic acid, by heating 2 parts of milk-sugar and 4 of nitric acid, spec. grav. 1·42, till a violent action commenced, then cooling, and heating again gently.

Mucic acid. relations.—*Neutral mucate of potassa*, obtained by saturating the acid with potassa or carbonate of potassa, is deposited from a boiling solution in white crystalline grains, which when dried in the air or at 100°, have the formula $2\,KO, C_{12}\,H_8\,O_{14}+HO$ (the water escapes at 150°); the mother-liquor assumes a brown colour, even if carefully purified mucic acid be employed; upon addition of a solution of nitrate of protoxide of silver, containing a little ammonia, and application of heat, metallic silver is deposited upon the sides of the vessel; the presence of saccharic acid, however, could not be proved. *Bimucate of potassa*, (dried *in vacuo* and at 100°: $KO, HO, C_{12}\,H_8\,O_{14}+2\,HO$), of which Hess denied the existence, is obtained by saturating a known weight of mucic acid with carbonate of potassa and adding an equal proportion of the acid; it forms small transparent crystals which are more easily soluble in water than the neutral salt.—*Neutral mucate of soda* crystallizes, on gradual evaporation of a solution of mucic acid neutralized with carbonate of soda, in large perfectly transparent crystals, $2\,NaO, C_{12}\,H_8\,O_{14}+9\,HO$, which effloresce in the air, and become, by heating to 100°, $2\,NaO, C_{12}\,H_8\,O_{14}+HO$. The latter salt separates on rapidly evaporating a solution of mucate of soda.—Solution of mucic acid is not precipitated by sulphate of magnesia. On mixing solutions of mucate of ammonia with sulphate of magnesia, a precipitate of *mucate of magnesia* is formed, which increases considerably in quantity by boiling the mixture; when dried at 100°, it is $2\,MgO, C_{12}\,H_8\,O_{14}+4\,HO$. Mucic acid behaves similarly with chloride of calcium; *mucate of lime*, dried at 100°, has the formula $2\,CaO, C_{12}\,H_8\,O_{14}+3\,HO$, and is soluble in acetic acid.—Mucic acid produces no precipitate with chloride of barium; on addition of ammonia, however, a crystalline precipitate separates, being deposited first on that portion of the vessel which has been scratched with the stirring-rod; *mucate of baryta*, thus obtained, and dried at 100°, is $2\,BaO, C_{12}\,H_8\,O_{14}+3\,HO$.—*Mucate of protoxide of copper* is obtained by precipitation of sulphate of protoxide of copper with mucate of ammonia; it is a bluish-white powder, insoluble in water, of the composition $2\,CuO, C_{12}\,H_8\,O_{14}+HO$, when dried at 100°.—*Mucate of protoxide of iron*, produced in a similar manner, is a yellowish-white powder, unchanged by exposure to the air, of the composition $2\,FeO, C_{12}\,H_8\,O_{14}+4\,HO$, when dried at 100°; exposed to a temperature of 150° to 160°, it becomes a brown mass, spontaneously inflammable in the air.—*Mucate of protoxide of lead*, obtained by precipitating a solution of mucic acid

with acetate of protoxide of lead, is a white granular powder, insoluble in water; dried at 100°, it is $2 PbO, C_{12} H_8 O_{14} + 2 HO$, at 150° it becomes anhydrous, and is in that state of a cinnamon-brown colour; Hagen's experiments do not confirm the statement that a portion of the acid may be withdrawn from this salt by ammonia. On addition of mucate of ammonia to basic acetate of protoxide of lead, a mucilaginous precipitate was obtained, slightly soluble in water, containing acetic acid and varying amounts of protoxide of lead (from 62 to 79 per cent). Hagen confirmed the formula, $2 AgO, C_{12} H_8 O_{14}$, for *mucate of protoxide of silver*, prepared with nitrate of protoxide of silver and mucate of ammonia. Mucic acid.

Camphoric Acid.—Blumenau(1) has made some communications respecting an acid obtained by him from camphor, by treating it with nitric acid, with application of heat, until white vapours appeared; it differed in its properties from common camphoric acid.

Kinic Acid. Kinone.—Woskresensky had fixed for kinone the relative atomic composition $C_3 H O$(2), and Wöhler the formula $C_{25} H_8 O_8$; Laurent adopted at a later period, the formula $C_{24} H_8 O_8$, agreeing with Woskresensky's determination. Wöhler(3) has since found the latter formula to correspond better with the composition of kinone, as well as with that of its products of transformation, than the one formerly adopted by him.

Astringent Extracts.—Guibourt(4) has published a comprehensive monograph on the astringent extracts occurring in commerce, under the names *catechu, gambir,* and *kino.*—Reinsch(5) has made communications on adulterated brown catechu (produced from the yellow by an admixture of alum).

Tannic Acid.—According to Pelouze, the lower of the two layers obtained in the exhaustion of galls by means of aqueous ether, is a solution of a quantity of tannic acid in water and the upper one a solution of a little tannic acid in ether. Mohr(6), on the contrary, states the lower layer to be a solution of tannic acid in ether, exhibiting the singular behaviour of not mixing with a farther quantity

(1) Ann. Ch. Pharm. LXVII, 119.

(2) Woskresensky has, contrary to Gerhardt's assertion (Compt. Rend. des Trav. Chim. 1849, 223), never deviated from this formula.

(3) Ann. Ch. Pharm. LXV, 349; Compt. Rend. XXVI, 121.

(4) J. Pharm. [3] XI, 24, 260, 360; XII, 37, 183, 267, (in abstr.); Repert. Pharm [2] XLVIII, 321.

(5) Jahrb. Pr Pharm. XVII, 201.

(6) Ann. Ch. Pharm. LXI, 352.

Tannic acid.

of ether; upon adding to a saturated etherial solution of tannic acid, a farther quantity of ether and then water, three strata are obtained, (the lower being an aqueous solution of tannic acid, the middle one an etherial solution, and the upper one ether, containing colouring matter and only a small quantity of tannic acid). He recommends the use of a mixture of equal volumes of alcohol and ether for the extraction of tannic acid.

Wetherill(1) found a mixture of sulphuric acid, spec. grav. 1·84, with 4 times its volume of water, to be most appropriate for the transformation of tannic into gallic acid; 500 cubic centimetres of that mixture are boiled with 50 grammes of dry tannic acid until the fluid crystallizes on cooling. He obtained from 100 parts of tannic acid as a maximum 87·4 of gallic acid. His analysis of tannic acid, dried at 110°, corresponds with the formula $C_{18}\,H_8\,O_{12}$; he, however, considers it probable that the formula $C_{14}\,H_6\,O_{10}$ is more correct, and that tannic acid is isomeric with gallic acid dried at 100° ($C_7\,H_3\,O_5$).

Mulder(2) also has published some researches on tannic acid. He views this acid, in the anhydrous state, as $C_{28}\,H_9\,O_{17}$. It required, according to him, a lengthened exposure to a current of dry air at 120°, in order to free it from hygroscopic moisture, it then had the formula $HO, C_{28}\,H_9\,O_{17}$, and lost about 3 per cent of water (calculated 2·8), if mixed with water and protoxide of lead and dried at 120°. By exposure of hydrate of tannic acid for some time to a current of ammonia, at the common temperature, and removal of the excess of ammonia by a current of air, a combination $NH_4\,O, C_{28}\,H_9\,O_{17} + 3\,NH_3$ was produced which, at 100°, assumed a brownish colour, and in that state had the composition $2\,NH_4\,O, C_{28}\,H_7\,O_{15}$, but if dried at 120° it became browner still, and had the formula $NH_4\,O, C_{28}\,H_8\,O_{16}$. Mulder endeavours to show that the earlier as well as the later analyses of tannates conducted under his superintendence, correspond with his view of the composition of the acid, for which purpose, however, he avails himself, at times, of rather complicated atomic proportions; he adopts five different salts of protoxide of lead (1 eq. of acid to $\frac{3}{2}$, 2, 3, 4, 5 PbO) and interprets a soda-salt, investigated by Büchner, as containing 4 eqs. of tannic acid to 5 of soda; the only salt which he mentions, as containing 1 eq. of acid to 1 eq. of base, is a potassa-salt, investigated by the chemist just mentioned.—He confirmed the statement

(1) J. Pharm. [3] XII, 107; J. Pr. Chem. XLII, 247.
(2) Scheikundige Onderzoekingen IV, 639; Repert. Pharm. [3] I, 311; II, 38.

of Pelouze, that the products of decomposition of tannic and gallic acids, by exposure to a continued heat, not exceeding 250^0, are water, carbonic acid, sublimed pyrogallic acid, and a residue of mellangallic acid; of the latter he obtained 53 to 58 per cent of the tannic acid employed. He likewise confirmed Pelouze's statement respecting the properties and composition of pyrogallic acid; he however considers $C_{40}\ H_{10}\ O_{14}$ as the probable expression for mellangallic acid, dried at 140^0, and KO, $C_{40}\ H_{10}\ O_{14}$ for the potassa-salt dried at 130^0, (obtained by digesting excess of the acid with potassa and evaporating the solution).—According to him the formation of the brown substance, which makes its appearance during the conversion of tannic into gallic acid, may be much checked by digesting tannic acid for several days with water and hydrochloric acid at 100^0, with perfect exclusion of the air. Tannic acid.

Wittstein(1) concludes from his experiments on the compounds of sesquioxide of iron with tannic acid, that the sediment which is gradually formed, in mixed solutions of tannic acid and sulphate of protoxide of iron, must be considered as a constant combination of 1 eq. of sesquioxide of iron with 4 eqs. of tannic acid, (the latter considered as $C_{18}\ H_8\ O_{12}$), but that, on the other hand, the precipitate produced in solution of sesquioxide of iron by means of tannic acid, is of varying composition.

Tannocaffeic Acid.—Rochleder has investigated the acids occurring in coffee, tea and paraguay tea. In an earlier memoir(2) he assigned to tannocaffeic acid, as contained in its combinations, the formula $C_{16}\ H_9\ O_8$, while Payen(3) ascribed to it the formula $C_{14}\ H_8\ O_7$; Rochleder(4) has since convinced himself of the correctness of the latter formula. He found(5) the same acid, combined with caffeine, in paraguay tea, (the leaves of *ilex paraguayensis*), and procured it by extracting this tea with alcohol of 40 vol. per cent, as long as the latter assumed a yellow colour, mixing the alcoholic extract with an alcoholic solution of acetate of protoxide of lead, until the precipitate formed was of a pure yellow colour, precipitating the filtered liquid completely by acetate of protoxide of lead, washing with alcohol the beautiful yellow precipitate obtained, suspending it in that liquid and decomposing it by hydrosulphuric acid. Rochleder has also investigated the alteration that tanno-

(1) Repert. Pharm. [2] XLV, 289.
(2) Ann. Ch. Pharm. LIX, 300.
(3) J. Pharm. [3] X, 266.
(4) Ann. Ch. Pharm. LXVI, 35; Wien. Acad. Ber. II, (1848), 224.
(5) Ibid. 39; Wien. Acad. Ber. II, (1848), 228.

Tanno-caffeic acid.

caffeic acid undergoes in the presence of bases by the influence of oxygen(1); with ammonia the result is different from that obtained with potassa or soda; if baryta or lime be present, the acid undergoes, at first, the same transformation as that produced by ammonia; this, however, soon changes into the alteration observed in the presence of potassa and soda. He has communicated a more detailed account with respect to the reaction in the presence of ammonia; he states that an acid is formed, which he calls *viridic acid,* and which he obtained in the following manner. A solution of pure tannocaffeic acid is prepared by exhausting dried and crushed coffee-beans with alcohol, mixing the extract with water, to separate the fatty matter, heating the filtered liquid to ebullition, precipitating with acetate of protoxide of lead, washing the precipitate and decomposing it by hydrosulphuric acid. This light-yellow solution, freed, by boiling, from hydrosulphuric acid, becomes dark-yellow on addition of an excess of ammonia, then greenish-yellow, by absorption of oxygen, after 36 hours, dark-bluish-green, and by lengthened standing, brown. Acetic acid converts the bluish-green into a chesnut-brown liquid, which, upon addition of alcohol, deposits black flakes, which are insoluble in dilute and pure alcohol, soluble in the alkalies, and form a black salt of protoxide of lead, on precipitation of the alkaline solution with the acetate. This substance resembles, in all its properties, the metagallic acid of Pelouze and the japonic acid of Svanberg; according to a single determination, its equivalent is 237. The brown liquid (which is changed immediately again to greenish-blue by saturation with a base) separated by filtration from the black flakes, produces with acetate of protoxide of lead a blue precipitate which, (washed with alcohol, and dried *in vacuo* and at 100^0), was found to correspond closely in composition to PbO, C_{14} H_6 O_7.—By extracting, with water, powdered coffee-beans (previously exhausted with alcohol), boiling the filtered liquid, precipitating with acetate of lead, decomposing the precipitate, suspended in alcohol, by hydrosulphuric acid, then mixing the resulting solution, filtered from the protosulphide of lead, with ammonia, and exposing it 24 hours to the air, adding alcohol and filtering off the greenish-blue precipitate that is formed; dissolving the latter in alcohol mixed with a little acetic acid, and precipitating the resulting brown solution with acetate of protoxide of lead, an indigo-blue compound was obtained, which, when dried at 100^0, had the composition

(1) Ann. Ch. Pharm. LXIII, 193.

$PbO, C_{14} H_7 O_8$. By decomposing this salt with hydrosulphuric acid and evaporating the solution, an amorphous mass is obtained, easily soluble in water, and dissolving in concentrated sulphuric acid with a carmine colour, from which solution it is precipitated by water in blue flakes. The brown liquid, filtered off from the protosulphide of lead, is immediately turned green by alkalies; with baryta-water it forms a bluish-green precipitate, which, dried at 100°, is $2 BaO, C_{14} H_8 O_9$. Coffee-beans owe their green colour to a small quantity of viridate of lime.—Tannocaffeic acid produces with potassa, on exposure to the air, a dark-brown solution, from which a brown potassa-salt, soluble in water, is precipitated by alcohol. Tanno-caffeic acid.

A second acid contained in coffee-beans, along with tannocaffeic acid, and first discovered by Pfaff, was obtained by Rochleder in the manner prescribed by the former chemist, by precipitating with acetate of protoxide of lead the aqueous decoction of coffee-beans (which had been previously treated with a little hot alcohol), decomposing the precipitate with hydrosulphuric acid, evaporating the filtered liquid to syrupy consistency, and then adding it to alcohol, when light flakes separated, which dried up to a loose powder; this acid appeared to contain carbon and water in the same proportion as tannocaffeic acid, but a larger proportion of oxygen.

Boheic Acid.—In a recent investigation of tea (of the leaves of *Thea bohea*) Rochleder(1) detected, besides common tannic acid, and a small quantity of a crystallizable acid, which was not more closely examined, a new acid which he called *boheic acid*. By precipitating a boiling decoction of tea-leaves with acetate of protoxide of lead, filtering, and separating the slight deposit formed in 24 hours, then neutralizing the fluid with ammonia, a precipitate was obtained. This precipitate suspended in alcohol was decomposed by hydrosulphuric acid, and the filtrate, from the resulting protosulphide of lead, freed from hydrosulphuric acid, and precipitated with an alcoholic solution of acetate of protoxide of lead;—a salt of protoxide of lead was thus obtained, which, dried at 100°, was found to have approximately the composition $PbO, C_7 H_5 O_6$; another salt was obtained in a similar manner (excepting that the last precipitation was effected by an ammoniacal solution of the acetate of lead), which, when dried at 100°, had the formula $2 PbO, C_7 H_4 O_5$. By precipitating, with baryta-water, the acid separated from the salt of protoxide of lead, and a baryta-salt, $BaO, C_7 H_5 O_6$, was formed. The acid itself,

(1) Ann. Ch. Pharm. LXIII, 202.

Boheic acid. evaporated and dried alternately at 100^0 and *in vacuo*, is a substance of pale yellow colour, when in a state of powder, which, at 100^0, fuses to a resinous red body; it is deliquescent in the air, soluble in water and alcohol, and has the composition $C_7\ H_5\ O_6$. One pound of tea yields no more than 1·5 grm. of pure boheate of protoxide of lead.

Angelic Acid.—Ricker and Reinsch(1) have shown the acid, discovered by the latter in the musk- or sumbul-root, and termed sumbulolic acid(2), to be identical, in its composition and physical properties, with angelic acid. For this acid, we refer also to "Roman Cumin-Oil."

Benzoic Acid.—Respecting the formation of benzoic acid, *see* "Decomposition of casein, &c., with sulphuric acid and binoxide of manganese, or bichromate of potassa."

Saint-Evre(3) has investigated various products of decomposition of benzoic acid. If 60 grammes of benzoic acid, and 200 of hydrate of potassa be dissolved in 300 to 350 of water, and a stream of chlorine passed through the liquid in the cold, it assumes successively the colours yellow, greenish-yellow, green, then once more yellow; at last a grey crystalline precipitate separates, carbonic acid being evolved during the whole operation. The precipitate consists of chlorate of potassa, a little unchanged benzoate of potassa, and the potassa-salt of a new acid; there remain, in the liquid, benzoate of potassa and chloride of potassium. The liquid is then increased to one and a half its bulk, by the addition of water, saturated with carbonic acid, and finally mixed with a little dilute hydrochloric acid, and the whole heated to ebullition, when the precipitate redissolves, and an oily fluid separates. This, removed from the liquid, solidifies upon cooling, to a hard, brittle, yellowish mass; it is freed from some adhering benzoic acid by repeated fusion in boiling water, and finally by recrystallization from alcohol, or from a mixture of alcohol and ether. The new substance is thus obtained in cauliflower-like groups of microscopic crystals; it fuses at 150^0, having in the fused state the spec. grav. 1·29, boils at 215^0, and is volatile without decomposition; its formula is $C_{12}\ H_5\ Cl\ O_4$; Saint-Evre calls it *chloroniceic acid.* Chloroniceate of protoxide of silver, $AgO, C_{12}\ H_4\ Cl\ O_3$, prepared from alcoholic solutions, separates in white flakes, which, by

(1) Jahrb. Pr. Pharm. XVI, 12; Ann. Ch. Pharm. LXVIII, 341.
(2) Ibid. XIII, 68.
(3) Ann. Ch. Phys. [3] XXV, 484; J. Pr. Chem. XLVI, 449; Compt. Rend. XXV, 912. (in abstr.); Compt. Rend. XXVII, 437.

washing and drying, become a crystalline powder. The baryta-salt is a white crystalline powder, corresponding in composition to the silver-salt, slightly soluble in water, tolerably so in hot alcohol, and decomposed by heat, with the formation of a solid and a liquid hydrocarbon and a carbonaceous residue. Chloroniceate of ammonia, when freshly prepared, by saturation of the alcoholic solution of the acid with ammonia, crystallizes in broad micaceous scales, of the formula NH_4O, $C_{12} H_4 Cl O_3$, which are fusible and volatile without decomposition, but when exposed to light, become brown and of an acid reaction. Chloroniceate of oxide of ethyl, $C_4 H_5 O$, $C_{12} H_4 Cl O_3$, is a colourless fluid, of the spec. grav. 0·981 at 10°, and boiling at 230°; its alcoholic solution, if left for some time in contact with ammonia, yields *chloroniceamide* NH_2, $C_{12} H_4 Cl O_2$, which crystallizes in large scales, of a greasy appearance, fusing at 100°.—Chloroniceic acid forms, with fuming sulphuric acid, another acid, the baryta-salt of which is soluble, and contains probably BaO, $C_{12} H_4 Cl O_3$, $2 SO_3$, HO.—Fuming nitric acid acts violently on chloroniceic acid, dissolving it; the solution deposits a substance which is soluble in alcohol, crystallizes in broad scales, of greasy appearance, and has the formula $C_{12} H_4 (NO_4) Cl O_4$, being chloroniceic acid, in which H is replaced by NO_4. The ether of this acid, $C_4 H_5 O$, $C_{12} H_3 (NO_4) Cl O_3$, crystallizes in colourless plates. On one occasion Saint-Evre obtained, by evaporation of the mother-liquor, from which $C_{12} H_4 (NO_4) Cl O_4$ had been separated, a substance, $C_{10} H_4 (NO_4) Cl O_4$, crystallizing in long white needles.—On distilling chloroniceic acid with excess of lime or baryta, a brownish-yellow liquid passes over at first, the action then appears to cease for a few moments; on continuing the application of heat, however, a lemon-yellow substance condenses in the neck of the retort, and a carbonaceous residue remains behind, from which water extracts a quantity of chloride of calcium. The fluid, which distils over first, is freed from the benzole it contains by exposure for some time to a stream of carbonic acid or hydrogen at 90°, it is then heated to from 290° to 295°, when a liquid passes over, which Saint-Evre calls *monochlorinated nicene*. It is of a faint amber-colour, its spec. grav. is 1·141 at 10°, its boiling-point 292° to 294°, and its composition $C_{10} H_5 Cl$. The observed density of its vapour is 7·2 to 7·5, the calculated density being 6·98 (for a condensation to 2 volumes). This liquid is violently acted upon by fuming nitric acid; after the action has ceased, alcohol of 36 vol. per cent is added, which dissolves the new substance, which is formed simultaneously with a resinous body; the latter, being the least soluble, separates first from the solution, and after

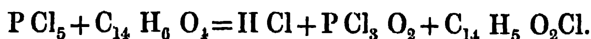
Benzoic acid.

Benzoic acid. one or two recrystallizations, the new compound $C_{10} H_4 (NO_4) Cl$ is obtained pure; it forms long, amber-yellow needles, of silky lustre, and is soluble in alcohol and ether. On dissolving this compound in alcohol, saturating the solution with ammonia, and submitting it to a stream of hydrosulphuric acid, it becomes brown, and subsequently assumes a dark violet-red colour; if no deposit should have formed after a few hours, the liquid is once more treated with ammonia and hydrosulphuric acid; it is then evaporated at the boiling temperature, and the residue treated with dilute hydrochloric acid and filtered; the golden-yellow filtrate deposits hydrochlorate of *chloronicine*, $C_{10} H_6 Cl N, HCl$, in yellowish prisms, grown together, generally, in groups of three and four; these are easily soluble even in cold water, and become brown when exposed to the air, being gradually decomposed. *Chloronicine*, $C_{10} H_6 Cl N$, is precipitated from the solution of the hydrochlorate, by ammonia, in brown flakes, which dissolve in an excess of water, but have no alkaline reaction, and are decomposed if allowed to remain for a lengthened period in the liquid. Acetate of chloronicine, (obtained by dissolving, in acetic acid, chloronicine which has been rapidly washed and dried, *in vacuo*, with exclusion of light), crystallizes in yellowish, four-sided prisms, which have an acid reaction and are altered by the action of light and moist air; the formula of this salt is $C_{10} H_6 Cl N, C_4 H_4 O_4$. The double salt of the hydrochlorate and bichloride of platinum, $C_{10} H_6 Cl N, HCl, Pt Cl_2$, forms a dark-yellow, granular precipitate.—Saint-Evre gives the name *paranicene* to a substance obtained by the distillation of chloroniceate of baryta, or chloroniceic acid, with lime or baryta; it is a solid, lemon-yellow hydrocarbon, of penetrating odour and taste, soluble in alcohol and ether, and crystallizing in broad plates; it is purified by pressure between bibulous paper, washing with a little cold ether and sublimation over freshly-ignited lime; its spec. grav. is 1·24, its boiling-point 365°, its composition $C_{20} H_{12}$; the observed density of its vapour 4·79, (calculated for a condensation to 4 volumes, it is 4·62). Paranicene is dissolved by fuming nitric acid, giving rise to a violent reaction; the solution deposits, on cooling, acicular crystals, soluble in alcohol and ether, of the composition $C_{20} H_{11} (NO_4)$. —By treating paranicene with ammonia and hydrosulphuric acid, in the manner described above, a substance is formed, which Saint-Evre has termed *paranicine*; it is precipitated by ammonia from the hydrochlorate in light yellow flakes, of the composition $C_{20} H_{13} N$; it is insoluble in water and soluble in ether; by dissolving it in the latter and evaporating the solution, an amber-yellow oil remains behind, which is soluble in hydrochloric acid, and reprecipitated by

Benzoic acid.

ammonia in white flakes. Hydrochlorate of paranicine crystallizes in octohedrons, which are decomposed by the action of the air, heat, and light, and have an acid reaction; the double salt with bichloride of platinum, $C_{20} H_{13} N, HCl, Pt Cl_2$, is obtained as a crystalline precipitate, scarcely soluble in ether.

By heating a mixture of pentachloride of phosphorus and well-dried benzoic acid, a fuming liquid distils over, which contains, according to Cahours(1), besides oxichloride of phosphorus and excess of the pentachloride, the chloride of benzoyl, discovered by Liebig and Wöhler. The latter is separated from the two former by distillation, that portion being reserved which passes over between 195° and 200°. Its specific gravity is 1·25 at 15°, its vapour-density 4·987, (calculated, for a condensation to 4 volumes, it is 4·901); its analysis furnished numbers corresponding with the composition of chloride of benzoyl; it forms, with alcohol benzoic ether, with ammonia benzamide, and with aniline benzanilide. The decomposition in this reaction is expressed by the equation:



$$P Cl_5 + C_{14} H_6 O_4 = H Cl + P Cl_3 O_2 + C_{14} H_5 O_2 Cl.$$

Pentachloride of phosphorus behaves with benzoate of potassa as it does with the uncombined acid. It has no action on benzoic ether.

By boiling benzoic acid with concentrated, or still better, with fuming nitric acid, nitrobenzoic acid, discovered by Mulder, is produced; it is benzoic acid in which 1 H is replaced by 1 (NO_4). By boiling benzoic acid with a mixture of fuming sulphuric and nitric acids for one hour, according to Cahours(2), 2 eqs. of hydrogen are replaced by 2 (NO_4), and *dinitrobenzoic acid* is formed. This substance is prepared by adding fused benzoic acid to the mixture of the acids, heated to from 50° to 60°; a slight evolution of gas takes place, while the benzoic acid dissolves. Heat is then gradually applied, until the fluid commences to become turbid, on cooling, the addition of water causes yellowish flakes to separate, which become white by being washed with water. As soon as the wash-water has no longer an acid reaction, the substance is pressed between bibulous paper and then dissolved in boiling alcohol, from which it separates, upon cooling, in small brilliant crystals. Dinitrobenzoic acid, $C_{14} H_4 (NO_4)_2 O_4$, thus obtained, fuses at a slightly elevated temperature, and sublimes without decomposition, by careful application of heat; it is scarcely soluble in cold, rather more so in boiling water, and pretty considerably so in alcohol and ether, it dissolves easily and

(1) Loc. Cit, p. 276. (2) Loc. Cit. p. 295.

Benzoic acid.

without decomposition in nitric acid, and also in concentrated sulphuric acid, when gently warmed, but is decomposed by application of too high a temperature. It forms soluble, crystallizable salts with potassa, soda, and ammonia, and slightly soluble salts with the protoxides of lead and silver; the salt of protoxide of silver, $AgO, C_{14} H_3 (NO_4)_2 O_3$, is white. Dinitrobenzoate of oxide of ethyl, $C_4 H_5 O, C_{14} H_3 (NO_4)_2 O_3$, is prepared by saturating boiling alcohol with dinitrobenzoic acid; the ether separates after some time, (and more plentifully on addition of water), as an oil which solidifies upon cooling; it crystallizes from an alcoholic solution, saturated while hot, in long, thin, brilliant needles, of a slight yellow tint.

Nitrobenzoic Acid.—Blumenau(1) states that dragon's blood, treated with nitric acid, spec. grav. 1·33 to 1·35, yields oxalic acid, and that with nitric acid, diluted with an equal weight of water, a non-volatile and a volatile acid are formed, of which the latter is identical with nitrobenzoic acid.

On warming nitrobenzoic acid with pentachloride of phosphorus, a heavy liquid, according to Cahours(2), distils over, which boils at between 265° and 268°; it is insoluble in water, and is decomposed, by a hot solution of potassa, into chloride of potassium and nitrobenzoate of potassa. Its formula is $C_{14} H_4 Cl NO_6 = C_{14} H_4 (NO_4) O_2 Cl$. it is therefore chloride of benzoyle, in which 1 H is replaced by 1 (NO_4). This new substance forms, with dry ammoniacal gas, a solid compound, crystallizing from water in yellow needles; it is probably identical with the substance Field obtained by heating nitrobenzoate of ammonia.

Cuminic Acid.—Cuminic acid is decomposed, according to Cahours(3), by distillation with pentachloride of phosphorus at 50° to 60°, with a plentiful disengagement of hydrochloric acid; oxychloride of phosphorus first distils over, and at 250° to 260° a colourless, mobile fluid, *chloride of cumyl*, $C_{20} H_{11} O_2 Cl$, is obtained. This substance boils at between 258° and 260°, has the spec. grav. 1·070 at 15°, is decomposed by exposure to moist air, and more rapidly by boiling it with potassa, into hydrochloric and cuminic acids; it forms with alcohol cuminic ether, with ammonia chloride of ammonium and cuminamide, and with aniline cuminanilide.

Cahours states(4) that cuminic acid dissolves, at a gentle heat, in fuming nitric acid, red vapours being evolved on boiling the solution;

(1) Ann. Ch. Pharm. LXVII, 127.
(2) Loc. Cit. p. 276.
(3) Ibid.
(4) Loc. Cit. p. 295.

Cuminic acid.

if, after a few minutes of continued ebullition, water be added, a heavy yellow oil separates, which soon solidifies; it is then washed with water, and crystallized from alcohol. This substance is *nitro-cuminic acid*, C_{20} H_{11} (NO_4) O_4 (cuminic acid in which 1 H is replaced by 1 NO_4); it crystallizes in yellowish-white needles, is insoluble in water, easily soluble in alcohol and ether, and forms crystallizable salts with the alkalies.—Upon adding fused cuminic acid, in small portions, to a mixture of sulphuric and nitric acids, gently warmed, it disappears, without any disengagement of gas, or violent action; on heating the fluid, red vapours are disengaged, and it suddenly becomes turbid; at this period a quantity of glittering crystalline scales separates from the liquid, which, by being washed with water, and recrystallized from alcohol, form lustrous plates. This substance has the composition of dinitrocuminic acid, C_{20} H_{10} $(NO_4)_2$ O_6, it is, however, not an acid.

Cinnamic Acid.—By heating pentachloride of phosphorus with cinnamic acid, Cahours(1) found the latter to undergo a decomposition analogous to that of benzoic acid; besides oxichloride of phosphorus and hydrochloric acid, a fluid was formed which boiled at 262°; it had the spec. grav. 1·207 at 16°, and proved to be *chloride of cinnamyl*, C_{20} H_7 O_2 Cl (cinnamon-oil, therefore, in which 1 H is replaced by 1 Cl). Chloride of cinnamyl is converted, by exposure to moist air, into hydrochloric and cinnamic acids; with alcohol, it forms cinnamic ether; with dry ammoniacal gas, chloride of ammonium, and a white crystallizable substance, analogous to benzamide. With aniline it forms cinnanilide (see "Aniline.")—By the repeated distillation of chloride of cinnamyle over protocyanide of mercury, or cyanide of potassium, there are formed protochloride of mercury, or chloride of potassium, and a liquid, containing still a little chlorine, and becoming brown when in contact with the air, with formation of hydrocyanic acid; this is cyanide of cinnamyl, C_{20} H_7 NO_2 = C_{18} H_7 O_2 Cy. The analysis made by Cahours of this substance, proves its existence, although the results obtained do not agree perfectly with the above formula.

Benzilic Acid.—The resultants of the treatment of benzilic acid with pentachloride of phosphorus, are, according to Cahours(2), hydrochloric acid, oxichloride of phosphorus, and a colourless liquid, of a strong odour, and boiling at 270°, which yields, with potassa, ammonia and aniline, products of decomposition corresponding to

(1) Loc. Cit. p. 276. (2) Ibid.

Anisic acid. those of the chlorides of benzoyl, cumyl, &c. It has the formula, $C_{28}H_{11}O_4Cl$, and has been named by Cahours, *chloride of benzile.*

Anisic Acid.—Cahours(1) states, that anisic acid dissolves easily in fuming nitric acid, when gently warmed; from this solution water precipitates nitranisic acid, in yellow flakes. If, however, the solution be heated to ebullition, carbonic acid is disengaged, and a product obtained, consisting of two substances, one of which is soluble in potassa, and has the composition of picric acid; while the other is insoluble in potassa, and likewise in boiling water. It is easily soluble in boiling alcohol and ether, and separates from this solution in the form of lustrous pale-yellow needles, which fuse at 85° to 86°, and may be sublimed, if carefully heated in close vessels. This substance is *dinitranisole*, $C_{14}H_6(NO_4)_2O_2$; it is not decomposed by a boiling dilute aqueous solution of potassa, and only after continued ebullition by a concentrated solution; an alcoholic solution of potassa decomposes it rapidly when boiled with it, forming a salt, which crystallizes in long orange-yellow needles, and from which Laurent's nitrophenesic acid, $C_{12}H_4N_2O_{10}$, is separated, by addition of nitric acid, or dilute hydrochloric acid.

Anisic acid dissolves in a mixture of fuming sulphuric and nitric acids, when slightly warmed, without colouring it; at a gentle heat carbonic acid is disengaged, and if the application of heat be continued until the liquid becomes turbid, and it be then left to itself, it separates into two strata. The upper one is oily, and solidifies on cooling; addition of water to the acid solution separates still more of this substance. It is almost insoluble in water (and may be purified thereby from the acid), soluble in hot alcohol, and still more easily in a mixture of equal parts of alcohol and ether, from which solution it crystallizes, by slow evaporation, in highly lustrous, slightly yellowish rhombic plates, fusing at 58° to 60°. It dissolves, at a gentle heat, without decomposition, in concentrated nitric and sulphuric acids. This substance is *trinitranisole*, $C_{14}H_5(NO_4)_3O_2$, and is likewise formed by the action of the mixture of fuming nitric and sulphuric acids, upon pure anisole.—Trinitranisole is not decomposed by a dilute solution of potassa, nor by concentrated ammonia, even at the boiling temperature, but becomes intensely brown by boiling with a moderately concentrated solution of potassa, a potassa-salt being formed, which is scarcely soluble in cold water, but crystal-

(1) Loc. Cit. p. 295; Compt. Rend. XXVII, 485, (in abstr.); Instit. 1848, 351.

lizes, on cooling from its solution in much boiling water, in long needles of a golden-chesnut-brown colour; the composition of this salt is $KO, C_{12} H_2 N_3 O_{13}$. From this compound, *picranisic acid*, $C_{12} H_3 N_3 O_{14}$, is separated by dilute nitric acid; it crystallizes from a hot saturated aqueous solution, on cooling, in yellow lustrous needles; it is slightly soluble in cold, and easily soluble in boiling water, in alcohol, and ether; it is isomeric with picric acid, but differs from the latter in its crystalline form, its solubility, its fusing-point, and in the physical properties of several salts. With ammonia it forms a salt of the formula, $NH_4 O, C_{12} H_2 N_3 O_{13}$, which crystallizes in long needles, sometimes of a yellow colour, with a feeble shade of orange, sometimes red, like bichromate of potassa; it frequently changes colour by recrystallization. Protoxide of silver dissolves in this acid; the silver-salt is deposited from the solution, by slow evaporation, in fine orange-yellow needles. The soda-salt crystallizes in long golden-yellow needles, and is much more soluble than the potassa-salt. The baryta- and strontia-salt form yellow, silky, difficultly soluble needles. Anisic acid.

Salicylate of oxide of methyl, which is isomeric with anisic acid, undergoes a different decomposition by the action of the mixture of fuming sulphuric and nitric acids. (See "Salicylate of oxide of methyl").

Cahours(1) found that, by the action of pentachloride of phosphorus on anisic acid, hydrochloric acid, oxichloride of phosphorus, and *chloride of anisyl*, $C_{16} H_7 O_4 Cl$, are produced. The latter is a colourless fluid, of a strong odour, its spec. grav. is 1·261 at 15°, its boiling-point 262°; it is decomposed, by moist air, into hydrochloric and anisic acids, and produces, with alcohol or pyroxylic spirit, the respective ethers, and with ammonia anisamide.

Nitranisic Acid.—Nitranisic acid produces, according to Cahours(2), when acted upon by pentachloride of phosphorus, besides oxichloride of phosphorus, a substance which has not been closely examined; it boils only at a very high temperature, is decomposed, by damp air, into hydrochloric and anisic acids, forms, with alcohol, anisic ether, and is, therefore, probably, *chloride of nitranisyl* $C_{16} H_6 (NO_4) O_4 Cl$.

Anilic Acid.—According to Hofmann(3), anilic acid is transformed into chloranile, by treatment of an aqueous solution with

(1) Loc. Cit. p. 276.
(2) Ibid.

Anilic acid.

chlorate of potassa and hydrochloric acid; the same effect, according to Stenhouse, is produced by the continued action of chlorine, with the aid of heat; on boiling a solution of the acid with hypochlorite of lime, it becomes dark-brown, and hydrochloric acid precipitates a yellowish, uncrystallizable resin.

Picric Acid.—With respect to the acid, discovered by Schunck among the products of the oxidation of aloes by nitric acid, formerly called by him chrysolepic acid, and considered isomeric with picric acid, he himself(1), as well as Marchand(2), Mulder(3), and E. Robiquet(4) have pointed out that, when pure, it is identical with picric acid. Marchand found both substances to possess an equal degree of solubility (100 water dissolve 0·626 at 5^0, 1·161 at 15^0, 1·225 at 20^0, 1·292 at $22·5^0$, 1·380 at 26^0, 3·89 at 77^0), and the same form of crystallization; the so-called nitrophenisic acid is likewise identical with these substances.

Blumenau(5) considers it probable, that picric acid is eventually decomposed, by very long continued boiling with nitric acid.

Chloropicrin.—If, according to Stenhouse(6), an aqueous solution of picric acid be mixed, in a retort, with hypochlorite of lime, an elevation of temperature ensues, and if the mixture be heated to ebullition, a colourless heavy oil distils over, along with water. The same substance is likewise formed, on boiling picric acid with chlorate of potassa and hydrochloric acid (when a residue of chloranile remains in the retort), or boiling with nitrohydrochloric acid (used only in small quantities), likewise by heating picrate of potassa with hypochlorite of lime, or by the long-continued action of chlorine upon a hot solution of picric acid. Styphnic and chrysamic acids behave like picric acid, but chloranile could by no means be transformed into this oily substance. Stenhouse calls it chloropicrin; he purifies it by washing, drying with fused chloride of calcium, and careful rectification in a water-bath. The substance, thus obtained, is a colourless oil, of highly refractive power, and the spec. grav. 1·6657; when diluted, it has a peculiar aromatic odour, and, if

(1) Ann. Ch. Pharm. LXV, 234.
(2) J. Pr. Chem. LXIV, 91.
(3) Scheikund. Onderzoek. IV, 506.
(4) J. Pharm. [3] XIV, 179.
(5) Ann. Ch. Pharm. LXVII, 115.
(6) Phil. Mag. [3] XXXIII, 53; Ann. Ch. Pharm. LXVI, 241; J. Pr. Chem. XLV, 56; Laurent and Gerhardt's Compt. Rend. Compt. des Trav. Chim. 1849, 35. In the latter journal Gerhardt expressed his opinion, that the true formula of chloropicrin might probably be $C_2\ Cl_3\ N\ O$, and since then (Laur. and Gerh. Compt. Rend. des Trav. Chim. 1849, 170), he has published some analyses by Cahours, which certainly agree with this formula for chloropicrin. Cahours found its boiling-point to be 114^0 to 115^0.

concentrated, violently attacks the nose and eyes; it is almost insoluble in water, but dissolves freely in alcohol and ether; it is not attacked by sulphuric, nitric, or hydrochloric acids, but is gradually decomposed by an alcoholic solution of potassa (with formation of chloride of potassium and nitrate of potassa); it is scarcely affected by aqueous solutions of the alkalies, but is decomposed, with explosion, on being warmed with potassium; it boils at 120°, and is not decomposed even at 150°, but on passing its vapour through a glass tube, heated above that temperature (but not actually red-hot), chlorine and binoxide of nitrogen are disengaged, and solid sesquichloride of carbon, C_4Cl_6, is deposited in the cooler portions of the tube. Stenhouse found the formula of chloropicrin to be, $C_4Cl_7N_2O_{10}$, he did not take into consideration a small quantity of hydrogen (0·22 to 0·26 per cent) obtained by analysis. Chloropicrin.

Nitro-bichlorophenic Acid.—Laurent and Delbos(1) obtained *nitro-bichlorophenic acid*, $C_{12}H_3Cl_2NO_6$, by passing chlorine into that portion of coal-naphtha which boils between 180° and 200°, then acting with nitric acid upon the same substance, washing the product with water, neutralizing with ammonia, boiling with water, filtering, adding nitric acid to the filtrate, and recrystallizing from alcohol the substance which separates upon cooling. This acid crystallizes in oblique rhombic prisms, of which the lateral planes are inclined towards each other at about 88°, and the terminal towards the lateral planes at from 108°·20′ to 108·30′; it is of a yellow colour, slightly soluble in water, but tolerably soluble in boiling alcohol and ether; when rapidly heated in a close vessel it is decomposed, with emission of light. The ammonia-salt, NH_4O, $C_{12}H_2Cl_2NO_5$, crystallizes in orange-red needles, which, if carefully heated, are partly volatilized without decomposition; the potassa-salt crystallizes in glittering scales, which appear, when viewed under different angles, either crimson or golden-yellow; when anhydrous, their formula is, $KO, C_{12}H_2Cl_2NO_5$.

Chrysamic Acid.—Mulder(2) and Schunck(3) have published researches on the acid which is found amongst the products of oxidation of aloes by nitric acid, and was called, by the latter chemist, chrysamic acid.

(1) Ann. Ch. Phys. [3] XIX, 380; J. Pr. Chem. XL, 382.

(2) Scheikund. Onderzoek. IV, 456; Repert. Pharm. [3] II, 62, 145; Ann. Ch. Phys. [3] XXII, 122, (in abstr.); J. Pharm. [3] XIII, 140; Ann. Ch. Pharm. LXVIII, 339; J. Pr. Chem. XLII, 250; Phil. Mag. [3] XXXII, 236.

(3) Ann. Ch. Pharm. LXV, 231; J. Pharm. [3] XIII, 299.

Chrysamic acid.

Mulder found the formula of chrysamic acid, dried at 120°, to be, $C_{14} H_2 N_2 O_{12}$, and the composition of the anhydrous neutral salts (for instance, the potassa-salt), dried at 120°, to be represented by the formula, MO, $C_{14} H N_2 O_{11}$. When dried in the air, the neutral soda-salt contains 3 eqs. of water, the magnesia- and potassa-salts 6; those of protoxides of manganese and lead (the latter formed by digesting chrysamic acid with neutral acetate of lead at 80°) contain 5 eqs. of water, and the salt of protoxide of copper 4 eqs.; all these salts are anhydrous, when dried at 155°. The neutral baryta-salt, dried at 110°, still contains 2 HO; the salt of protoxide of lead, formed from chrysamate of potassa, and neutral acetate of protoxide of lead, is, 2 PbO, $C_{14} H N_2 O_{11}$. Chrysamic acid is converted, by exposure to a stream of dry ammoniacal gas at 100°, into *chrysamide*, $C_{14} H_4 N_3 O_{11}$, which may be combined with bases, and produces, f. i., by the addition of its solution to acetate of protoxide of lead, a combination, PbO, $C_{14} H_4 N_3 O_{11} + 3$ HO (dried in the air).

Schunck found that the yellow powder, formed by the action of nitric acid on aloes, consists of two acids, aloetic acid and chrysamic acid, and that the former may be transformed into the latter by treating it with strong nitric acid; he determined the composition of aloetic acid to be $C_{16} H_4 N_2 O_{13}$. He calls *chrysaminamide* the substance which separates, after boiling chrysamic acid with an aqueous solution of ammonia, from the cooling liquid, in the form of needles, appearing reddish-brown by transmitted and greenish by reflected light; the analytical results obtained correspond equally well with the two formulæ $C_{28} H_{10} N_7 O_{21}$ and $C_{30} H_{10} N_7 O_{23}$. By adding hydrochloric acid or dilute sulphuric acid to a hot aqueous solution of this substance, Schunck obtained, on the cooling of the liquid, needles which, after washing and drying, were of a dark olive-green colour, and had the composition $C_{15} H_4 N_3 O_{11}$ or $C_{15} H_4 N_3 O_{12}$; he calls this substanee *amido-chrysamic acid*. A solution of this acid in ammonia gave, upon addition of chloride of barium, a red crystalline precipitate; it is transformed, by boiling with nitric acid, into chrysamic acid, the supernatant liquid containing nitrate of ammonia; on treatment with caustic potassa it yields ammonia; with water a dark-purple solution, from which it is partially precipitated by strong acids, without changing to yellow, (as is the case with chrysamic acid). Its salts resemble the chrysamates, and detonate like them upon being heated, but when treated with caustic potassa, they yield ammonia; they are likewise produced from chrysaminamide by addition of ammonia

(on addition of chloride of barium and ammonia to an aqueous solution of chrysaminamide, the chrysamate of baryta is precipitated immediately; without addition of ammonia, however, this salt does not separate at all in the cold, and only gradually on boiling, chloride of ammonium then remaining in solution).—Chrysamic acid, when warmed with a moderately concentrated solution of potassa, dissolves, without disengagement of ammonia, to a brown fluid, which becomes darker during ebullition and parts with carbonic acid, which goes over to the potassa, chrysamic acid ceasing to be in solution; at this point, acids produce in it a dark-brown precipitate, which is not soluble in water containing an acid, but dissolves in pure water, forming a brown solution, which is precipitated by acids and salts of the alkalies. By boiling chrysamic acid with a strong solution of potassa, and adding chloride of barium, a brown precipitate is obtained, which, when treated with a little sulphuric acid, yields a brown liquid, containing baryta, and leaving, upon evaporation, a brown residue, which consists of minute plates of the composition $BaO, C_{12} H_4 N_2 O_9$ (the nitrogen was not determined); Schunck considers the acid in this baryta-salt to be the same as that termed by him aloëresinic acid.—Chrysamic acid forms with a boiling solution of sulphide of potassium, containing an excess of potassa, an intensely blue fluid, from which, upon cooling, needles separate, appearing blue by transmitted and copper-red by reflected light; they yield, when dried, a mass of indigo-blue almost black colour, and may be purified by recrystallization from a boiling solution of potassa. Schunck calls this new substance *hydrochrysamide;* it does not detonate when heated; it gives off violet vapours, when heated in a test-tube, which condense to blue crystals, while the greater portion of the substance is decomposed, with disengagement of ammonia and formation of a carbonaceous residue; it is insoluble in water, and slightly soluble in alcohol, which it colours faintly blue; it is soluble in concentrated sulphuric acid and reprecipitated in blue flakes from this solution, by water; in caustic potassa and carbonate of potassa it dissolves with a blue colour, and is precipitated from such solutions by acids; the results of analysis agree equally well with the two formulæ $C_{14} H_6 N_2 O_6$ and $C_{30} H_{12} N_4 O_{13}$. This substance is likewise formed by the action of chrysamic acid on a boiling solution of protochloride of tin, which immediately assumes a blue colour. Hydrochrysamide is decomposed* by chlorine and boiling nitric acid. In the decomposition by the Chrysamic acid.

Chrysamic acid. latter, nitrous acid is evolved, a dark-brown liquid being obtained, which yields, on evaporation, a brown syrup. On treating this with water, there remains a brown powder, which dissolves in carbonate of potassa, giving a brown solution, and resembles the substance formed by the action of potassa on chrysamic acid; the liquid, which is separated from the brown powder, contains oxalic acid and ammonia.

Constitution of the Acids $C_n H_n O_4$.—Frankland and Kolbe(1) are of opinion that the acids $C_n H_n O_4$ (in the so-called hydrated state, *n* representing a whole number) might be considered as conjugate compounds of oxalic acid with hydrogen, methyl, ethyl, and so on, f. i.

Formic acid.	Acetic acid.	Metacetonic acid.	Butyric acid.
$H, C_2 O_3, HO$	$C_2 H_3, C_2 O_3, HO$	$C_4 H_5, C_2 O_3, HO$	$C_6 H_7, C_2 O_3, HO$.

Considering benzoic acid ($C_{14} H_6 O_4$) to be likewise a conjugate oxalic acid (phenyl-oxalic acid, $C_{12} H_5, C_2 O_3, HO$), and believing that the combinations, termed nitriles, had to be more correctly viewed as cyanogen-compounds (benzonitrile $C_{14} H_5 N_1$, for instance, as cyanide of phenyl $C_{12} H_5 Cy$), they conjectured that, as the cyanide of phenyl is converted into phenyl-oxalic acid, so likewise methyl-oxalic-, ethyl-oxilic-, and amyl-oxalic acids, *i. e.* acetic, metacetonic and caproic acids, might be prepared from cyanides of ethyl, methyl and amyl. The results of their experiments on this subject fulfilled their expectations; an account of them will be given below under the heads of the last named acids.

Acetones of the Acids $C_n H_n O_4$.—Chancel(2) has endeavoured to support the view that every acetone (according to the hitherto adopted views $C_{n-1} H_{n-1}O$) of an acid $C_n H_n O_4$ is composed of the aldehyde of this acid ($C_n H_n O_2$) and the hydrocarbon of the preceding series ($C_{n-2} H_{n-2}$); that common acetone, (of acetic acid) f. i., the formula of which is $C_6 H_6 O_2$, should be written $C_4 H_4 O_2 + C_2 H_2$.

Sources of the Acids $C_n H_n O_4$.—Du Menil(3) has called attention to the occurrence of volatile acids in wormwood- and lavender-water, and to the difference between the properties of their combina-

(1) Ann. Ch. Pharm. LXV, 288; J. Pr. Chem. XLVI, 301, in abstr.; Phil. Mag. [3] XXXI, 266, in part (particularly the statements respecting cyanide of ethyl and metacetonic acid); Chem. Soc. Mem. III, 386; J. Pr. Chem. XLII, 313; J. Pharm. [3] XIV, 294.

(2) J. Pharm. [3] XIII, 468.

(3) Arch. Pharm. [2] LI, 18.

tions with protoxide of zinc and those of valerianate of protoxide of zinc.—In the product of distillation of the milfoil (yarrow) blossoms (*achillea millefolium*), which had the odour of butyric and valerianic acids, Krämer(1) found metacetonic acid; in the distillate from carraway he found acetic acid, and in those obtained from *Tanacetum vulgare, Arnica montana* and *Rosa centifolia* he discovered acids of an odour similar to that of butyric and valerianic acids.—The fruit of the soap-tree (*Sapindus saponaria*), when distilled with water and sulphuric acid, yielded a product containing, according to Gorup-Besanez(2), formic and butyric acids. Tamarinds, treated in the same manner, yielded formic and acetic acids; the distillate had likewise the odour of butyric acid, the existence of this acid could, however, not be decidedly proved. Gorup-Besanez considers it probable that the above-mentioned acids are formed by the oxidation of tartaric acid originally contained in this fruit.—Böhme(3) has shown that, amongst the products of putrefaction in peas and lentiles, metacetonic and butyric acids are more particularly formed.—According to Dessaignes and Chautard(4), metacetonic acid is probably contained in spent tan, besides butyric acid. (*See* the articles on the respective acids).

Sources of the acids $C_n H_n O_4$.

Respecting the formation of formic, acetic, metacetonic and caproic acids, compare also "Decomposition of casein, fibrin, &c., by means of sulphuric acid and binoxide of manganese or bichromate of potassa."

Formic Acid.—On the occurrence of formic acid in fruits, compare above. Some observations and experiments, with respect to the formation of this acid in oil of lemons, have been published by F. Müller(5); he does not, however, himself consider that they suffice to afford information respecting the acid which is formed in oil of lemons.

Fr. Will(6), of Erlangen, has shown the active poisonous principle in the caterpillar, especially in the *bombyx processionca,* to be formic acid. It exists in a free, concentrated state in all parts of the caterpillar, but particularly in the *fæces,* likewise in the greenish-

(1) Arch. Pharm. [2] LIV, 9.
(2) Gel. Anz. d. bair. Acad. Nr. 232; Ann. Ch. Pharm. LXIX, 369; J. Pr. Chem. XLVI, 151.
(3) J. Pr. Chem. XLI, 278; Ann. Ch. Pharm. LXIV, 328, (in abstr.)
(4) J. Pharm. [3] XIII, 244; J. Pr. Chem. XLV, 49.
(5) Arch. Pharm. [2] LI, 149.
(6) Froriep's Notizen, VII, 141.

Formic acid.

yellow matter that exudes when the caterpillar is cut, and in the hollow bristles.

Cloez(1) recommends, for the preparation of dilute formic acid, that a mixture of 500 grm. of wheat-starch with 2000 grm. of binoxide of manganese, be mixed with 1 litre of water, in a still of from 20 to 30 litres' capacity, that 2 kilogrammes of sulphuric acid, diluted with 2 litres of water, be then added and the mixture distilled, hot water being added to the mixture during the process, in the same amount as it distils over; he states that from 12 to 15 litres of a very acid liquid may be thus obtained, containing about 412 grm. of hydrate of formic acid.

Bineau(2) obtained needle-shaped crystals from a solution of neutral formiate of potassa in hot concentrated formic acid, on its cooling; the mother-liquor yielded, by exposure *in vacuo* over sulphuric acid and caustic potassa, a crystalline mass, a portion of which was retained *in vacuo* as long as it emitted the odour of formic acid, while the other portion was dissolved in alcohol and the solution evaporated to dryness *in vacuo;* all these three products contained potassa and formic acid in the proportion shown by the formula $KO, C_2 H O_3 + H O, C_2 H O_3$; the first contained 2·6, the second 7·6, and the third 11·0 per cent of water, in addition to the water expressed by the formula. A solution of formiate of soda in concentrated formic acid gave, by exposure *in vacuo,* indistinct crystals, of a similar composition, and containing acid and base as represented by the formula $NaO, C_2 H O_3 + H O, C_2 H O_3$, besides 7 per cent of water.—Both these salts possess a very acid taste, are exceedingly deliquescent, and are converted, for the greater part, into neutral salts, by solution in much water and evaporation; they lose a portion of their acid by lengthened exposure *in vacuo.*

Acetic Acid.—On the occurrence of acetic acid, *see* page 419, Bastick(3) has made some communications on the formation of this acid in tinctures.

According to Frankland and Kolbe(4), cyanide of methyl (obtained, though not free from hydrocyanic acid, by distilling dry sulphomethylate of potassa with cyanide of potassium, and rectifying the product over chloride of calcium), forms acetate of potassa, with a

(1) J. Chim. Méd. [3] IV, 306.
(2) Ann. Ch. Phys. [3] XIX, 291, and (the same memoir) XXI, 183; J. Pr. Chem. XL, 354.
(3) Pharm. J. Trans. VII, 268.
(4) Loc. Cit. p. 418.

considerable disengagement of ammonia, upon being treated for some time with a boiling, moderately concentrated, aqueous solution of potassa, in an apparatus so arranged that the volatilized portion condenses and returns to the solution of potassa. Acetic acid.

Dumas, Malaguti and Leblanc(1) likewise observed the formation of acetic acid by the action of an aqueous solution of potassa on cyanide of methyl; they obtained the latter by removing the elements of water from acetate of ammonia (*see* the Nitriles), and also by the action of dry cyanide of potassium upon sulphate of oxide of methyl; when prepared by the latter process, it contained some cyanide of ammonium and formiate of ammonia in admixture, which impurities imparted to it an insupportable odour and taste, as well as poisonous properties; they were removed by boiling, first with protoxide of mercury, and afterwards with anhydrous phosphoric acid.

According to Taddei(2), a solution of potassa, of 1·06 spec grav., added drop by drop to a boiling solution of neutral acetate of protoxide of lead, of the spec. grav. 1·25 to 1·30, the liquid being agitated, produces for a long time no permanent precipitate; suddenly, however, the whole liquid solidifies to a white mass, consisting of a double salt, moderately soluble in hot water, consisting of 3 PbO, 2 KO, 3 $C_4 H_3 O_3$, besides water.

Wittstein(3) has examined the spontaneous decomposition which *liquor ferri acetici oxydati*, and *tinctura ferri acetici ætherea Klaprothii* undergo, when depositing, after some time, a brown gelatinous precipitate. He has arrived at the conclusion, that this precipitate may be considered as a superbasic acetate of sesquioxide of iron, but that it was of inconstant composition, inasmuch as the amount of acid it contained varied with the acidity of the solution from which it was deposited; that the decomposition was not attended by the formation of protoxide of iron, but that by exposure of the solutions to diffused light, the latter might be produced, and exert an accelerating influence on the decomposition, the real cause of which was, however, as yet unknown.

Aldehyde.—Weidenbusch(4) has investigated the action of alkalies and acids upon aldehyde. He likewise was unsuccessful in obtaining, in a state of purity, the yellow resin, which separates,

(1) Compt. Rend. XXV, 474.
(2) Chem. Gaz. 1848, 169, from Raccolta Fisico-chimica Italiana, II, 562.
(3) Repert. Pharm. [3] I, 289.
(4) Chem. Gaz. 1849, 34; Ann. Ch. Pharm. LXVI, 152; J. Pr. Chem. XLVI, 252; Laurent and Gerhardt's Compt. Rend. des Trav. Chim. 1849, 28.

Aldehyde. accompanied by the disengagement of a pungent odour, during the action of potassa upon aldehyde;—because it could not be freed from the substance to which this odour is due, this being a volatile, oleaginous body, thickening readily when in contact with air, and more readily by the action of nitric acid, to a golden-yellow, viscous resin, of a cinnamon-like odour, soluble in alcohol and ether, and also somewhat soluble in water, but differing from the real aldehyde-resin. The latter is a dark orange-yellow powder, becoming paler by desiccation at 100°, which is soluble in alcohol and ether, slightly so in water, but scarcely at all in alkalies, and only partially in concentrated sulphuric acid; it is reprecipitated from the latter solution by water. It is rapidly deprived of its colour by passing only a little chlorine into its alcoholic solution, from which it is reprecipitated by water as a snow-white powder, containing, however, some chlorine. The most highly purified resin was found to contain 76·4 per cent of carbon, and 8·0 per cent of hydrogen; its formation is attended by the production of acetic, formic, and aldehydic acids (acetylous acid), which combine with the potassa.—If aldehyde be brought in contact, at a temperature below 0°, with a minute quantity of sulphuric, or nitric acid, small acicular crystals soon separate, which are probably infusible metaldehyde; on agitating the supernatant liquid with water, a fluid separates, and rises to the surface, which, when dried by chloride of calcium, and rectified, has the composition $C_{12} H_{12} O_6$, and the same vapour-density (4·583) as elaldehyde, but a higher boiling-point (125°) than it; it is reconverted into aldehyde when *warmed* with a trace of sulphuric, or nitric acid; it changes rapidly by itself, or in the presence of water, to an acid, the baryta-salt of which is crystallizable, and easily soluble in water; it reduces salts of protoxide of silver with facility, and yields, with salts of the sub- and protoxide of mercury, white precipitates; (heat decomposes the precipitate obtained with salts of the suboxide, a reduction of the suboxide to metal being effected; while that produced in salts of the protoxide remains white even when boiled).

A mixture of aldehyde and water being exposed, for some time, to a current of hydrosulphuric acid, became turbid, a semi-fluid clear oil separating, which was dried *in vacuo*. Its spec. grav. is 1·134, it has the offensive odour of garlic, is somewhat soluble in water, and easily so in alcohol and ether; it is miscible with fatty and etherial oils, and agrees in composition with the formula $C_{12} H_{13} S_7$; it commences to boil at 180°, but the boiling-point rises continually, the oil becoming brown; there remains in the retort, finally, a brown

viscid substance, which solidifies into a mass of crystals. By chloride of calcium this oil is decomposed into sulphide of calcium and aldehyde; with ammoniacal gas, it produces thialdine. The addition of a single drop of concentrated sulphuric acid (or the exposure to a current of hydrochloric acid gas) causes it to solidify to a white crystalline mass, while hydrosulphuric acid is evolved. This mass dissolves upon addition of more sulphuric acid, and may be reprecipitated by water; it is soluble in alcohol and ether, and slightly so in water; it distils over with the latter, and crystallizes in dazzling white needles, of a disagreeable garlic-odour; these commence to sublime at 45°, and have the formula, $C_{12}H_{13}S_7 - HS = C_{12}H_{12}S_6$, or $C_4H_4S_2$; this substance is, therefore, aldehyde, in which the oxygen is replaced by sulphur (Weidenbusch calls it *acetyl-mercaptan*). There are other methods of obtaining this compound from the oil, $C_{12}H_{13}S_7$; f. i., it is formed by heating the oil (in fact, the crystalline body remaining behind on its distillation is acetyl-mercaptan); likewise, by exposing water saturated with the oil to the air, hydrosulphuric acid being evolved; (the oil may be reproduced by passing a current of that gas into this solution); by lengthened exposure of the oil over sulphuric acid, under a bell-jar, or by the action of a small quantity of chlorine, (much of the latter produces an oily fluid, with a most disagreeable odour). The compound, $C_4H_4S_2$, is neutral in its properties, it is not acted upon by ammonia, potassa, and protoxide of mercury; it effervesces violently when nitric acid is poured upon it. On mixing alcoholic solutions of this substance, and of nitrate of protoxide of silver, a pretty considerable white precipitate is formed, which rapidly changes in colour, and, on being heated, deposits protosulphide of silver, while a silver-compound remains dissolved in the hot alcohol. If this solution be filtered, while boiling, nacreous spangles separate on cooling, which, when washed with alcohol, correspond in composition to the formula, $2(AgO, NO_5) + 3C_4H_4S_2$; they possess the odour of acetyl-mercaptan, (which substance may be separated from them by alkalies); they darken on exposure to light, when heated alone, they blacken, evolving nitrous acid, and are decomposed, on evaporation of their aqueous solution, with deposition of protosulphide of silver. Aldehyde.

Respecting the aldehydes of other acids (metacetonic and butyric acids), *see* "The decomposition of casein, &c., by sulphuric acid and binoxide of manganese, or bichromate of potassa."

Metacetonic Acid.—On the occurrence of metacetonic acid, compare page 419.

The acid, detected by Nöllner, in the fermented mother-liquor of

Metacetonic acid. acid tartrate of potassa, termed pseudo-acetic acid by him, and butyro-acetic acid by Nicklès (who found it to have the formula, $C_6 H_6 O_4$, but believed it to differ from metacetonic acid), has been proved by Dumas, Malaguti, and Leblanc(1), to be identical with metacetonic acid. Both acids, besides possessing the same composition, are also identical in their appearance, odour, and boiling-point (which is about 140°). They form the same salts of baryta, and of protoxide of silver; the former, prepared with both acids, has been investigated crystallographically by Provostaye. The above-named chemists propose for this acid the name of *propionic acid* (first fatty acid), as it is the first of the series $C_n H_n O_4$ that exhibits the character of a fatty acid, *i. e.* in being separated from its solution as a layer of oil, and in forming salts with the alkalies, which have a greasy feel. Dumas, Malaguti and Leblanc produced this acid by the action of potassa upon cyanide of ethyl(2). They obtained metacetonate of potassa as a white salt of nacreous lustre, very soluble in water; the silver-salt, obtained from the former compound by precipitation with nitrate of protoxide of silver, was found to possess the formula AgO, $C_6 H_5 O_3$. They observed, in the separation of metacetonic acid from the potassa-salt, by distillation with syrupy phosphoric acid, that the portion of the acid which passes over last, crystallizes and remains solid at the common temperature, if protected from moisture.

Frankland and Kolbe(3) obtained metacetonic acid in the same manner. They prepared cyanide of ethyl by distilling sulphovinate of potassa with cyanide of potassium, agitating the product with water, separating it from the latter by chloride of sodium, drying it with chloride of calcium, and rectifying it; when pure it is a fluid of the spec. grav. 0·7889 at 12°·6, and boiling at 80°; it is, contrary to Pelouze's statement, considerably soluble in water, from which it may, however, be nearly perfectly separated by addition of chloride of sodium or chloride of calcium.—On treating cyanide of ethyl with a boiling aqueous solution of potassa, the evaporating liquid being allowed to condense and return to the flask, metacetonate of potassa was obtained, and this salt, when distilled with sulphuric acid, yielded aqueous metacetonic acid. The baryta-salt of the latter crystallizes with difficulty; when dried at 100° it has the formula BaO, $C_6 H_5 O_3$; the salt of protoxide of silver separates in small crys-

(1) Compt. Rend. XXV, 781; Ann. Ch. Pharm. LXIV, 329 (in abstr.)
(2) Ibid. 656.
(3) Loc. Cit. p. 418.

talline scales from a hot saturated solution, on its cooling; it is less soluble in water than the acetate, and, when dried *in vacuo* over sulphuric acid, has the composition assigned to it by Gottlieb, $AgO, C_6 H_5 O_3$; the salt of protoxide of lead has a sweet taste, its solution leaves, on evaporation, a tenacious gummy mass, which, dried *in vacuo* over sulphuric acid, is $PbO, C_6 H_5 O_3$.

Nitrometacetonic acid.

Respecting the metacetonic acid, in which hydrogen is replaced by chlorine, we refer to page 384.

Nitrometacetonic Acid.—According to Laurent and Chancel(1), if a mixture of equal volumes of butyrone ($C_7 H_7 O$) and nitric acid of the usual strength, be gently heated, a violent action ensues, nitrous vapours and carbonic acid being evolved; if the application of heat be discontinued as soon as the action commences and the fluid be poured into a large quantity of water, after the evolution of gas has ceased, an oily liquid is precipitated, which mixes in all proportions with alcohol; this substance is *nitrometacetonic acid,* being metacetonic acid, in which 1 H is replaced by 1 NO_4. It may be obtained in a state of greater purity by the addition of a strong acid to an aqueous solution of the potassa- or ammonia-salt; it remains fluid even at a very low temperature, it is inflammable and possesses an aromatic odour and a sweet taste. On mixing alcoholic solutions of the acid and of potassa, yellow needles of the potassa-salt are immediately formed; they are purified by recrystallization. The ammonia-salt is produced in a similar manner; the other salts, and especially the silver-salt, are obtained by double decomposition. All these salts are crystallizable, and, with the exception of the ammonia-salt, take fire with a kind of explosion, when gently heated. The formula of the acid is $HO, C_6 H_4 (NO_4) O_3$, that of the crystallized potassa-salt is $KO, C_6 H_4 (NO_4) O_3 + 2 HO$. The ammonia-salt, which is isomorphous with the former, having the formula $NH_4 O, C_6 H_4 (NO_4) O_3 + 2 HO$, sublimes without decomposition, but, when kept for several days, it spontaneously explodes; hydrosulphuric acid decomposes it with deposition of sulphur. The solution of the potassa-salt yields with nitrate of protoxide of silver a yellow precipitate, probably a basic-salt; on treating this with boiling water, there remains a residue of protoxide of silver, and the neutral silver-salt is dis-

(1) J. Pharm. [3] XIII, 462; Compt. Rend. XXV, 883; Ann. Ch. Pharm. LXIV, 331.

Butyric acid.

dissolved, crystallizing in rhombic plates of the formula AgO, $C_6H_4(NO_4)O_3+2HO$.

Butyric Acid.—On the occurrence and formation of butyric acid, *see* p. 393 and 419.

Wackenroder(1) has shown that some butyric acid is formed during the conversion of sugar of milk into lactic acid.

Bensch(2) has pointed out that, in Gobley's method for the preparation of lactic acid, there is no means of ascertaining when the conversion of the sugar into lactic acid is completely effected, and that a loss of that acid may hence arise, in consequence of the production of butyric acid (which commences immediately after the formation of lactic acid).—Bensch gives the following directions for the preparation of lactic and butyric acids. 6 pounds of cane-sugar and ½ ounce of tartaric acid are dissolved in 26 pounds of boiling water, and the solution allowed to stand for several days; about 8 ounces of old putrid cheese broken up in 8 pounds of skimmed and curdled sour milk; 3 pounds of levigated chalk are then added, the mixture being placed in a warm place, at about 30^0 to 35^0, and well stirred daily. After 8 or 10 days, the whole solidifies to a magma of lactate of lime, which is then mixed with 20 pounds of boiling water and ½ ounce of caustic lime, boiled for half an hour, strained through a filter-bag, and the filtrate evaporated to syrupy consistency; after four days the lactate of lime will be found to have separated in crystalline grains. It is then drained, mixed up, three or four different times, with about $\frac{1}{10}$th of its weight of cold water, and drained by pressure; it is now dissolved in twice its weight of boiling water, 3½ ounces of sulphuric acid, diluted with an equal weight of water, being added to the solution for every pound of the pressed lactate of lime contained therein; the precipitate formed is filtered off, and the hot filtrate boiled for a quarter of an hour (not longer) with carbonate of protoxide of zinc, in the proportion of $1\frac{3}{8}$ pound to every pound of sulphuric acid employed; the liquid, filtered while boiling, deposits, after some time, colourless lactate of protoxide of zinc in crystallized crusts, which are washed with cold water, dissolved in 7½ times their weight of boiling water, and decomposed by hydrosulphuric acid.

If the above mixture of sugar, chalk, &c., is left for a longer period than ten days at 35^0, the water, evaporated, being replaced,

(1) Arch. Pharm. [2] LI, 138. (2) Ann. Ch. Pharm. LXI, 174.

the mass becomes again more liquid, while gas is evolved, and after five or six weeks, the lactic acid is entirely converted into butyric acid. The liquid obtained is mixed with an equal volume of cold water, a solution of 8 pounds of crystallized carbonate of soda added, and the precipitated carbonate of lime filtered off and washed; the filtrate and wash-waters are evaporated down to 10 pounds, when 5½ pounds of sulphuric acid, previously diluted with an equal weight of water, are carefully added. The butyric acid, which separates on the surface of the liquid, as a dark-coloured oil, is removed, and the rest of the liquid distilled; the distillate is neutralized with carbonate of soda and the butyric acid it contains, likewise separated by sulphuric acid. The whole of the crude butyric acid is rectified, with the addition of 1 ounce of sulphuric acid to every pound; the distillate is saturated with chloride of calcium, which removes the acetic acid, and redistilled; the first portion that comes over is dilute butyric acid, containing traces of hydrochloric acid, the latter portion is concentrated butyric acid. 28 ounces of pure concentrated butyric acid are thus obtained from 6 pounds of cane-sugar. Butyric acid.

According to Laroque(1) butyric acid may be distinguished from valerianic acid by the latter forming, when added to a solution of acetate of protoxide of copper, at first a green oily stratum floating on the surface of the liquid, and a solid precipitate only upon agitation, while the latter is produced immediately by butyric acid(2). Laroque observed that the crystallized *butyrate* of *protoxide of zinc* fused at about 100°, and was decomposed at higher temperatures, with evolution of acid vapours and the formation of an anhydrous salt and butyrone; he also found that the anhydrous salt fused at 140°, and that by boiling a solution of this salt butyric acid was volatilized, an insoluble basic salt being formed. — *Butyrate* of *protoxide of copper*

(1) From Recueil des Trav. de la Soc. d'Émulat. pour les Sc. Pharm., Janvier, 1847, in J. Pharm. [3] XII, 67.

(2) It may here be stated, that the separation of butyric from valerianic acid, is effected by semi-saturating a mixture of the acids with carbonate of soda, and distilling; the product consists entirely, or principally, of butyric acid, according to the proportion in which the acids are mixed; if the distillate contains valerianic acid, the residue in the retort will be found quite free from butyric acid; in the other case, the residuary soda-salt is decomposed by sulphuric acid, the acid; thus separated, is once more semi-saturated with carbonate of soda, distilled, and so on; the last distillation will yield products gradually richer in pure valerianic acid.

Butyric acid. was found by Lies(1) to be represented by the formula CuO, $C_8 H_7 O_3 + HO$.

Valerianic Acid.—On the occurrence of valerianic acid, *see* p. 419.

Thirault(2) agrees with the view, that valerianic acid does not pre-exist in the valerian-root, but is formed by the oxidation of the oil contained therein, by the oxygen of the atmosphere, and, that water and caustic alkalies promote this oxidation, although the latter have no direct chemical action on valerian-oil. He recommends that the separation of the acid from the roots be not proceeded with, until they have been boiled in a weak aqueous solution of an alkali, and exposed therein to the action of the atmosphere for a month.—Leudet(3) found, that no valerianic acid was formed by exposure of the oil in the presence of water to the atmosphere; he believes, on the contrary, that, under these circumstances, a different acid is formed, separating, on the addition of nitric acid, from its aqueous solution as a resinous substance.

Lefort obtained, by following Brun-Buisson's direction for the preparation of *valerianate of zinc*, with some slight modifications of his own (by macerating, for twenty-four hours, 4 kilogrammes of valerian-root with 25 litres of water, 400 grammes of sulphuric acid, and 240 grammes of bichromate of potassa, then distilling off 10 litres, and saturating the distillate with protoxide of zinc) an abundant product of a zinc-salt, which consisted, however, chiefly of sulphate of protoxide of zinc. According to Lefort's observation, valerianate of zinc is decomposed by boiling its aqueous solution.—Larocque(4), likewise, found this to be the case; he also states that it is more difficult to obtain a volatile anhydrous salt from the valerianate of protoxide of zinc than from the butyrate; and that the former salt, when distilled, has the appearance of paraffine.—Wittstein(5) has observed, that the aqueous solution of valerianate of zinc is rendered turbid, by being heated for a short time, becoming, however, clear again on cooling; but that, after continued ebullition, it deposits a basic salt, which does not redissolve on cooling.

(1) Compt. Rend. XXVII, 321.
(2) J. Pharm. [3] XII, 161; Repert. Pharm. [2] XLVII, 389.
(3) Ibid. [3] XI, 444.
(4) From Recueil des Trav. de la Soc. d'Émulat. pour les Sc. Pharm., Janvier, 1847, 44 in J. Pharm. [3] XII, 68.
(5) Repert. Pharm. [3] I, 189.

Wittstein also found, that on mixing a thin paste of freshly precipitated carbonate of protoxide of zinc, with valerianic acid, a salt $ZnO, C_{10} H_9 O_3 + 12 HO$ is formed, containing water which is not expelled at 50°, but is evolved at 100°; while the salt that separates on evaporation of an aqueous solution, or on mixing solutions of sulphate of protoxide of zinc and valerianate of soda, is anhydrous; the salt containing water is soluble in 44 times, and the anhydrous salt, according to later experiments, in 90 times its weight of water. Valerianic acid.

Wittstein(1) formerly assigned to *valerianate* of *sesquioxide of iron*, the formula $3 Fe_2 O_3, 7 C_{10} H_9 O_3 + 2 HO$. Rieckher(2) considered this salt, obtained by him on adding a solution of sesquichloride of iron to a moderately warm solution of valerianate of soda, as an amorphous lustrous substance, dark-red and translucent at the edges, and brittle at the common temperature, to contain merely hygroscopic water (to the extent of 17 per cent); his analysis of the salt, dried at 100°, corresponds with the formula $3 Fe_2 O_3, 7 C_{10} H_9 O_3$. Wittstein(3) endeavoured to prove the correctness of his formula by new analyses, and stated, that at 100° this salt gradually lost almost the half of its acid. Rieckher(4), at a later period, considered it probable that the substance, obtained by him, was different from that formed on addition of an alkaline valerianate to a solution of sesquioxide of iron in the cold; and that, without regarding the water in the former, which he considered as hygroscopic, its composition was expressed by the formula $4 Fe_2 O_3, 9 C_{10} H_9 O_3$.

Wittstein(5) has found the valerianate of teroxide of bismuth, (obtained as a loose white powder, by the addition of valerianate of soda to a solution of bismuth in nitric acid, and by nearly perfect saturation with carbonate of soda), when dried at 50°, to have the formula $3 Bi O_3, 2 C_{10} H_9 O_3 + 4 HO$.

Decomposition of Valerianic Acid by the Electric Current.— Kolbe(6) has investigated the decomposition of valerianic acid by the electric current. By the action of a current produced by six pairs of Bunsen's carbon-zinc battery, the electrodes being of platinum, and immersed in a concentrated solution of valerianate of potassa, at 0°, hydrogen, carbonic acid and a new

(1) Repert. Pharm. [2] XXXVII, 300.
(2) Jahrb. Pr. Pharm. XV, 151.
(3) Jahrb. Pr. Pharm. XVI, 324.
(4) Ibid. XVII, 85.
(5) Repert. Pharm. [3] I, 37.
(6) Chem. Soc. Mem. III, 378; Phil. Mag. [3] XXXI, 348; J. Pr. Chem. XLII, 311; Ann. Ch. Pharm. LXIV, 339 (in abstr.)

Decomposition of valerianic acid by the electric current.

gaseous hydrocarbon were evolved, and a light oily liquid separated, which rose to the surface, the potassa being finally converted principally into the neutral and acid carbonates. The light oily fluid, possessing an etherial odour, is a mixture of two substances; one of these is decomposed by an alcoholic solution of potassa, with formation of valerianate of potassa. (Kolbe supposes this substance to be an etherial combination $C_8 H_9 O$, $C_{10} H_9 O_3$; but operating with very small quantities he did not succeed in isolating the new alcohol $C_8 H_{10} O_2$, which must be formed by the decomposition of this compound). The other substance is a light colourless oily fluid, of an agreeable aromatic odour, boiling at 108°; its spec. grav. is 0·694 at 18°, and its composition $C_8 H_9$, its vapour-density is 4·05 (with the assumption of a condensation to 2 volumes, it is calculated at 3·94). Kolbe calls this liquid *valyl;* its formation from valerianic acid, with the evolution of carbonic acid and hydrogen, is explained by the equation $C_{10} H_{10} O_4 = C_8 H_9 + 2 CO_2 + H$. Valyl is soluble in alcohol and in ether, but not in water, and is not affected by oxygen or iodine, while bromine, chlorine, and fuming nitric acid convert it into products of substitution.—The gaseous hydrocarbon, formed during the decomposition of valerianic acid, possesses a peculiar etherial odour, its formula is $C_8 H_8$, and its spec. grav. double that of olefiant gas; with chlorine it forms, even in the dark, a heavy oily fluid, containing several substitution-products.—Kolbe has likewise observed that acetic and butyric acids are decomposed in a similar manner; the former yielding only gaseous products, the latter, also a volatile liquid, $C_6 H_7$(1).

According to Frankland and Kolbe(2), cyanide of amyl, [which, when obtained pure in a manner similar to that for cyanide of ethyl, (p. 424), is a mobile liquid of peculiar odour, of the spec. grav. 0·8061 at 20°, having a vapour-density of 3·333, (calculated at 3·351 for a condensation to 4 volumes), boiling at 146°, and less soluble in water than cyanide of ethyl, but miscible in all proportions with alcohol] yields caproate of potassa, when treated with an alcoholic solution of potassa (which acts more rapidly than an aqueous solution), in such a manner that the evaporated liquid returns to the potassa. To confirm this decom-

(1) Kolbe has given a more detailed account of this reaction, in a memoir lately published (1849) Ann. Ch. Pharm. LXIX, 257.

(2) Loc. Cit. p. 418.

position, the combinations of this acid with baryta and protoxide of silver were prepared and analysed. Fatty acids in oil of cocoa-nut.

Fatty Acids in Oil of Cocoa-Nut.—Fehling(1) had pointed out, at an earlier period, the existence of caproic acid, $C_{12} H_{12} O_4$, and caprylic acid, $C_{16} H_{16} O_4$, in cocoa-nut oil; A. Görgey(2) has found, besides these, capric acid, $C_{20} H_{20} O_4$. The principal constituent of cocoa-nut oil is, however, according to Görgey's experiments, Sthamer's pichurim-stearic acid (lauro-stearic acid of Marsson $C_{24} H_{24} O_4$). Görgey could not obtain an acid of the formula $C_{22} H_{22} O_4$, such as Saint-Evre(3) asserts that he has discovered; he considers it however probable that myristic acid $C_{28} H_{28} O_4$, and palmitic acid $C_{32} H_{32} O_4$, exists in cocoa-nut oil, besides the acids already enumerated. Capric and pichurim-stearic acids may be recognized, according to Görgey, amongst the mixture of fatty acids in cocoa-nut oil, by the behaviour of their baryta-salts during crystallization from the hot aqueous solution; the latter becomes turbid on cooling, even while passing through the filter, and deposits white flakes, which are pichurim-stearate of baryta. The supernatant liquid soon becomes turbid again, caprate of baryta being deposited as a fine white powder. Baryta-salts of the acids of atomic weights lower than that of caprylic acid ($C_{16} H_{16} O_4$) may be easily obtained by means of baryta-water, but with the acids of higher atomic weight it is better to precipitate the ammonia-salts with chloride of barium. Should the mixture of acids contain caprylic acid, its presence may be recognized by the liquid, filtered from the precipitate produced by chloride of barium, becoming opalescent, (like a dilute solution of ammonia-soap), after being rapidly boiled down and cooled.

The following are some additional statements made by Görgey respecting capric and pichurim-stearic acids.

Capric acid.—This acid is contained only in small quantities

(1) Ann. Ch. Pharm. LIII, 390; Berzelius' Jahresber. XXVI, 619.

(2) Ann. Ch. Pharm. LXVI, 290; Ann. Ch. Phys. [3] XXV, 102.

(3) Saint-Evre has given the name *cocinic acid* to the substance obtained from cocoa-nut oil, by saponifying the latter, separating the acids from the soap, pressing and recrystallizing them from alcohol, resaponifying with soda, precipitating the soda-compound with acetate of protoxide of lead, extracting the lead-compounds with ether, and decomposing the residue with tartaric acid; the analyses of the crystallized acid (the fusing-point of which was 347°), and its combinations with oxide of ethyl and protoxide of silver, led him to the formula, $C_{22} H_{22} O_4$; the product of dry distillation of the lime-salt (cocicone) yielded, on analysis, numbers corresponding with the formula; $C_{21} H_{21} O$. (Ann. Ch. Phys. [3] XX, 91; J. Pr. Chem. XLI, 144; Ann. Ch. Pharm. LXIV, 341 (in abstr.)

Fatty acids in oil of cocoa-nut.

in cocoa-nut oil. It fuses at 30° and possesses a faint hircinic odour; it is perceptibly soluble in hot water but separates again, on cooling, in lustrous crystalline spangles, so perfectly indeed, that the water scarcely retains any acid reaction. The baryta-salt crystallizes in delicate dentritic aggregates, on evaporation of its aqueous solution to a pellicle.

Pichurim-stearic acid.—On cooling an alcoholic solution of this substance, saturated at the ordinary temperature, down to 0°, it is deposited in concretions of the size of a hazel-nut, consisting of small spicular crystals. Its spec. grav. is 0·883 at 20°, its fusing-point lies between 42° and 43°.—Pichurim-stearate of oxide of ethyl, $C_4 H_5 O, C_{24} H_{23} O_3$, solidifies at — 10°; it has the spec. grav. 0·86 at 20°, and the boiling-point 264° (coinciding accurately with the calculated boiling-point, according to H. Kopp's law); the spec. grav. of its vapour, observed, is 8·4, the calculated number is 7·9.—Pichurim-stearate of baryta is deposited from its hot aqueous solution in small white flakes; 1 part of this salt is soluble in 10864 parts of water at 16·5°, in 1982 parts at 100°, in 1468 parts of common alcohol at 15·5°, and 211 parts of alcohol at the boiling temperature.

Fatty Acids in Castor-Oil.—According to the earlier investigations of Bussy and Lecanu(1), castor-oil was considered as a combination of oxide of glyceryl with three fatty acids, of which the one fusing at 130°, was called margaritic acid; while the two others, existing as liquids, were named ricic and elaiodic acid. Bussy and Lecanu consider the two latter to be identical with the acids appearing among the products of the dry distillation of castor-oil.

Saalmüller(2), in again taking up this investigation, has shown that castor-oil contains no acid fusing at 130°, and that the high fusing-point and the difficult solubility in alcohol of margaritic acid, as observed by the above named chemists, is to be ascribed to its retaining a portion of alkali. He found the fusing-point of this acid to be 70°, and its point of solidification between 68° and 70°. One analysis of the substance furnished numbers corresponding exactly with the formula of stearic acid; three other analyses, however, made with substance of a different preparation, gave results more closely agreeing with the composition of palmitic acid. It, therefore, still remains doubtful whether all kinds of castor-oil contain invariably the same solid fatty acid, and like-

(1) J. Pharm. XIII, 57.
(2) Ann. Ch. Pharm. LXIV, 108, (in abstr.); J. Pharm. [3] XIII, 391.

wise which acid it is; invariably, however, its relative proportion in the oil is very insignificant. Fatty acids in castor-oil.

The principal portion of the fatty acids, obtained by the saponification of castor-oil, consists of an acid, which, at the common temperature, is of syrupy consistence, of a pale sherry colour, and inodorous, but of a disagreeable sharp and acrid taste; its spec. grav. is 0·94 at 15°, it only solidifies at from —6° to —10°, to a mass of globular concretions. The best method for obtaining it pure is that described by Gottlieb for the preparation of the indesiccative oleic acid.

Saalmüller calls this substance *ricinoleic acid.*—It is miscible in all proportions with alcohol and ether, its solution has an acid reaction, and decomposes the alkaline carbonates. It is not affected by contact with oxygen, and yields, on distillation, no sebacic acid, but œnantholc and œnanthylic acid, as shown by Bussy.—According to Saalmüller, the composition of ricinoleic acid is expressed by the formula $C_{38}\ H_{36}\ O_6 = HO,\ C_{38}\ H_{35}\ O_5$. The ricinoleates of the alkaline earths and the heavy metallic oxides, that have been examined, are almost all crystallizable; they are all soluble in alcohol and some also in ether; they are anhydrous after desiccation *in vacuo,* with exception of the lime-salt, and have the formula MO, $C_{38}\ H_{35}\ O_5$. Like the acid itself, they do not absorb oxygen from the air. The following salts were obtained by precipitation of aqueous solutions of the chlorides with a very dilute solution of the acid in an excess of ammonia: the baryta-salt, (crystallizing from its alcoholic solution in white, delicate laminæ); the strontia-salt, (crystallizing in small white grains); and the lime-salt, (forming small dazzling white scaly crystals, which contain 1 eq. of water and fuse at 80°). The magnesia-salt crystallizes in thin needles; the salt of protoxide of zinc, in small white nodules. The salt of protoxide of lead could not be obtained of constant composition by precipitating a solution of the acid in an excess of ammonia, with acetate of protoxide of lead, but was prepared perfectly pure by digesting the acid with an excess of protoxide of lead at a gentle heat, and recrystallizing the resulting combination from ether; it fuses at 100°. It was likewise difficult to obtain a salt of protoxide of silver of constant composition. Ricinoleate of oxide of ethyl is a sherry-coloured oily fluid, which cannot be distilled without undergoing decomposition.

Saalmüller has also found that, contrary to the statements made

Fatty acids in castor-oil.

by Boudet(1), neither castor-oil nor ricinoleic acid are at all altered in composition or physical constitution by treatment with sulphurous acid.

Svanberg and Kolmodin(2) obtained different results in their investigation of the liquid acid of castor-oil. After saponification of the oil, the acids were precipitated by hydrochloric acid, washed, and the more solid ones separated by filtration at from 3^0 to 5^0. That portion which passed through the filter was treated with ammonia in an insufficient quantity to neutralize it; the resulting soap was decomposed with chloride of barium and the baryta-salt recrystallized from alcohol until it contained a constant amount of baryta. Svanberg and Kolmodin deduced, from a single analysis of this salt, the formula BaO, $C_{36} H_{33} O_5$; according to them pure ricinoleic acid (precipitated from the baryta-salt by hydrochloric acid), is a weak acid, solidifying at about 0^0, the alcoholic solution of which scarcely reddens litmus paper.

The solid acids of castor-oil have been likewise examined by Scharling(3). Some crystals, which had been deposited from castor-oil, were repeatedly dissolved in boiling alcohol; from the cooling solution a fat separated, which fused at 44^0, and yielded by saponification a fatty acid, fusing at 72^0. After saponifying the oil, from which the crystals had been deposited, decomposing the soda-compound with acetate of protoxide of lead, and treating the precipitate obtained, with ether, there remained a lead-compound; the acid of which, after repeated recrystallization from alcohol, likewise fused at 72^0. The analysis of the silver-salt corresponded nearly to the composition of palmitate of protoxide of silver, AgO, $C_{32} H_{31} O_3$, Scharling considers its correct formula to be AgO, $C_{32} H_{32} O_3$, and views the acid it contains as a peculiar ricinostearic acid, which is distinguished from palmitic acid by its higher fusing-point (the latter fusing at 60^0), and from common stearic acid, by its somewhat greater volatility.

Œnanthole.—Bussy(4) found, at an earlier period, amongst the products of distillation of castor-oil, a peculiar fluid, boiling at from 155^0 to 158^0, which he called œnanthole; he assigned to it the

(1) Ann. Ch. Phys. [2] L, 391; Berzelius' Jahresber. XIII, 284.

(2) From Oefversigt af Kongl. Vetensk. Förhandl. 1847, 124, in J. Pr. Chem. XLV, 431.

(3) Oversigt over det Kongl. danske Vidensk. Selsk. Forhandl. 1847; Trier und Faber's Archiv for Pharmacie og technisk Chem. II, 25; J. Pr. Chem. XLV, 434.

(4) Compt. Rend. XXI, 84.

formula, $C_{14}H_{14}O_2$, and described the method of obtaining it pure. Williamson, and Tilley have submitted this substance to farther investigations. Œnanthole.

Williamson(1) confirmed Bussy's formula of œnanthole, and found its boiling-point to be at from 155° to 156°.—On treating œnanthole with a concentrated aqueous solution of potassa, an elevation of temperature ensued, the odour of the supernatant liquid was altered, and there was found, in combination with the potassa, an acid, separable as an oil by tartaric acid; this was recognized as being œnanthylic acid (the baryta-salt, BaO, $C_{14}H_{13}O_3$, and the salt of protoxide of silver were submitted to analysis); the composition of the oil, formed in this reaction (as the residuary substance, after treating œnanthole with potassa), was found to vary very much in different preparations; it differs, moreover, from œnanthole by yielding, with nitric acid, a product heavier than water, while the latter yields, by the same treatment, an agreeably smelling product, which is lighter than water.—After treating œnanthole, dissolved in four times its volume of alcohol, with hydrochloric acid gas, addition of water separates an oil, differing from œnanthole, which may be distilled with water, or even by itself, if the temperature be properly regulated; it is a colourless fluid, of an agreeable odour, and was recognized as being œnanthylate of oxide of ethyl, $C_4H_5O, C_{14}H_{13}O_3$.—The results of the action of chlorine upon œnanthole are hydrochloric acid, and a semi-fluid oil of an agreeable odour, which is heavier than water; it may be distilled by itself, and has the formula, $C_{14}H_{11}Cl_3O_2$. In Williamson's opinion, the formula of œnanthole ought to be doubled, and this substance considered as a sort of ether, $C_{28}H_{28}O_4 = C_{14}H_{13}O + C_{14}H_{13}O_3$, whereby the formation of œnanthylic acid by the action of potassa, or hydrochloric acid, might be explained.

Tilley(2) likewise found Bussy's formula of œnanthole to be correct, and its boiling-point to be 155°; he observed that this substance became brown and acid, after lengthened ebullition, its boiling-point rising at the same time.—When œnanthole is added, drop by drop, to strong nitric acid, it is violently acted upon, the acid retains œnanthylic, caproic, and oxalic acids in solution, a mixture of œnanthylic and caproic acids, and *nitracrole* distilling

(1) Ann. Ch. Pharm. LXI, 38.

(2) Phil. Mag. [3] XXXIII, 81; Ann. Ch. Pharm. LXVII, 105; J. Pr. Chem. XLV, 306; J. Pharm. [3] XV, 237 (in abstr.)

Œnanthole

over. The latter substance was discovered by Redtenbacher, among the products of decomposition of choloidic acid, by nitric acid; it may be separated from the distillate, obtained by the action of nitric acid upon œnanthole, by the addition of water, in heavy drops, which unite to a colourless fluid, of a penetrating and irritating odour; on heating it with water to 100°, it is decomposed into nitrous acid and another substance, called by Redtenbacher cholacrole, which is a clear yellowish liquid, possessing, likewise, an intense odour when concentrated, and having, according to Redtenbacher, the composition $C_8 H_5 N_2 O_{13}$; it imparts a yellow colour to solution of potassa, forming with it crystals of nitrocholate of potassa, KO, $C_2 N_4 HO_9$ (discovered by Redtenbacher), while a heavy oil remains.—The production of œnanthylic and caproic acids, by the action of nitric acid upon œnanthole, was confirmed by the analysis of the baryta-salts, BaO, $C_{14} H_{13} O_3$, and BaO, $C_{12} H_{11} O_3$.—Tilley obtained œnanthylic acid by the action of fused potassa, as well as of an aqueous solution of the alkali upon œnanthole. On distilling the residuary oil, obtained in the latter case, with water, it passes over slowly, as a colourless liquid, possessing a feeble odour of lemons; it boils at 220°, undergoing partial decomposition; it is only slightly soluble in water, but dissolves in all proportions in alcohol and ether; it burns with a bright flame, and has the formula, $C_{14} H_{14} O$; Tilley calls it *hydride of œnanthyl.* The decomposition of œnanthole, by an aqueous solution of potassa, into œnanthylic acid and hydride of œnanthyl, is expressed by the equation: $3 (C_{14} H_{14} O_2) = C_{14} H_{14} O_4 + 2 (C_{14} H_{14} O)$. Hydride of œnanthyl yields, with nitric acid, œnanthylic acid, and, on being heated with potassa, œnanthylic acid and a pitch-like substance, while hydrogen is liberated.—By the action of ammonia-gas on œnanthole, *œnanthyl-ammonia* is produced; if sulphurous acid be passed through a solution of this compound in strong alcohol, *sulphite of œnanthyl-ammonia,* $C_{14} H_{13} O, SO_2 + NH_4 O, SO_2$, separates as a white crystalline powder (or upon employing a more dilute solution, in small distinct prisms); it is quite analogous to the sulphite of aldehyde-ammonia, discovered by Redtenbacher. Sulphite of œnanthyl-ammonia is slightly soluble in alcohol and water; when heated, it fuses, and white vapours are evolved, after which it blackens, and burns with a flame. It is gradually decomposed by contact with water, in the cold, and more rapidly when heat is applied, œnanthole being liberated, and bisulphite of ammonia remaining in solution; this decomposition proceeds still more rapidly in the presence of acids.

Dœglingtrain-Oil.—Scharling(1) has investigated the train-oil of the bottle-nose-whale of the Faroe Islands (the *Balæna rostrata* of Chemnitz, the hyperodon of later authors). This train-oil is a better fuel for lamps than the common train-oil, and has the spec. grav. 0·868. It may be freed from its bad odour by exposure, in contact with water, to the solar rays, by agitation with thin milk of lime, or by solution in boiling alcohol (1 part dissolving ½ part of the oil, 1 part of alcohol at 37° dissolving $\frac{1}{22}$ part). It absorbs oxygen, and becomes thereby heavier and more viscous. It is darkened and soon rendered solid by nitrous acid; on treating it then with alcohol, a crystalline substance, more difficultly soluble, may be separated, which dissolves in 10 times its weight of boiling alcohol, and fuses at 32°. At 8° this train-oil becomes turbid, and at a few degrees above 0°, it forms a semi-fluid mass. By exposing it for a lengthened period to a temperature of — 8°, and allowing the more fusible portion to flow off at gradually increased temperatures, a fat was finally obtained which fused at 24°, and contained amongst other substances some spermaceti; the fat was saponified, the soda compound exhausted with ether, and a silver-salt prepared from the residue, which had the composition AgO, $C_{20}\ H_{19}\ O_3$.

Dœgling-train-oil.

The principal mass of the train-oil consists of an oleic acid, which, according to Scharling, differs somewhat from common oleic acid. The train-oil was boiled with protoxide of lead and water, by which a compound was obtained, one portion of which was soluble, the other insoluble in ether. The insoluble portion yielded a fatty mass, consisting, for the greater part, of a substance fusing at 49°; and likewise of another body, in small quantity, which was decomposed at 100°, without fusing. The soluble portion, when treated with hydrosulphuric acid, yielded an acid which remained solid at a few degrees above 0°, and fused at 16° to a clear yellow liquid, which reddened litmus-paper. Scharling assigns to this acid the formula $C_{38}\ H_{36}\ O_4$, to the baryta-salt BaO, $C_{38}\ H_{35}\ O_3$, and to its combination with oxide of ethyl $C_4\ H_5\ O$, $C_{38}\ H_{35}\ O_3$; he calls it *dœglic acid.*—On rapidly distilling dœgling train-oil, there remains only a very slight residue; carbonic acid, carburetted hydrogen, and a very small quantity of acrolein are disengaged; the distillate is a bright fluid, consisting principally of several hydrocarbons. By digestion of this

(1) From Trier's Archiv. for Pharm. og technisk Chem. I, in J. Pr. Chem. XLIII, 257.

Dœgling-train-oil. product with carbonate of soda, rectification in a water-bath, desiccation with chloride of calcium, and redistillation over potassium, a liquid was obtained of the composition $C_{12}H_{12}$, which was found to have the density of vapour 5·8 which (assuming a condensation to 2 volumes) corresponds exactly with the calculated number. Scharling has given the name, *dœglic oxide,* to a compound of 2 eqs. of this hydrocarbon with 1 eq. of water; according to him, pure dœglingtrain-oil may be considered as dœglate of dœglic oxide.

Acid from Behen-Oil.—Walter(1) had stated that the behen-oil (from *Moringa aptera*) contains, besides margaric and some stearic acid, a peculiar solid acid, behenic acid $C_{30}\,H_{29}\,O_4$, fusing at 53°, and also a peculiar liquid substance, moringic acid, $C_{30}\,H_{28}\,O_4$, solidifying at 0°. Völcker(2) found in behen-oil (from *Moringa oleifera*), amongst other acids, one fusing at 60° (named by him behenic acid); he investigated its combinations with baryta, soda, oxide of ethyl and protoxide of lead, and likewise the acid in the crystalline state, to which he assigned the formula $C_{42}\,H_{42}\,O_4$. Strecker(3) has, however, shown that the results obtained by the analysis of the three first named compounds, and of the crystallized acid, agree better with the formula $C_{44}\,H_{44}\,O_4$.

Examination of the Fuel from an ancient Lamp.—Braconnot(4) examined the fuel found in an antique lamp, probably of the 4th century. It was partially soluble in boiling alcohol of 0·959° spec. grav.; the solution deposited, on cooling, a substance in white flakes, fusing at 64°, (probably cerin) which admitted of being partially saponified with potassa, and yielded a product from which margarate of potassa was extracted by alcohol in the cold; a white residue being left, which corresponded in its properties with ceraïn. The alcohol employed retained a substance in solution, which was obtained upon evaporation as a white, hard, brittle mass, fusing at 51°; its alcoholic solution reddened litmus-paper, and deposited, on slow evaporation, small granular crystals; Braconnot calls this substance *cerantic acid.*—The portion of the original substance which was insoluble in alcohol, contained myricin.

(1) Compt. Rend. XXII, 1143; Ann. Ch. Pharm. LX, 271; Berzelius' Jahresber. XXVII, 429.

(2) Scheikund. Onderzoek. III, 545; J. Pr. Chem. XXXIX, 351; Ann. Ch. Pharm. LXIV, 342; Berzelius' Jahresber. XXVII, 427.

(3) Ann. Ch. Pharm. LXIV, 346.

(4) Ann. Ch. Phys. [3] XXI, 484.

Fatty Substance from the Body of a putrified Animal.—Gregory(1) investigated the fatty mass, into which the body of a pig had been converted, with disappearance of the bones, by burial in a damp soil for the space of fifteen years. The substance was of a waxy nature; different portions yielded unequal amounts of ash (from 1·5 to 3·5 per cent — carbonate of lime); the mass consisted of about ¼ of stearic acid, and ¾ of margaric and oleic acids. Fatty substance from the body of a putrified animal.

Action of Sulphur and Heat upon Fatty Oils.—Anderson(2) has examined the products of decomposition obtained, by heat, from fatty oils in contact with sulphur. On warming a fatty oil with sulphur, the latter fuses, and is dissolved by degrees in the fat, forming a thick dark-red fluid. On increasing the temperature, a violent reaction ensues, much hydrosulphuric is evolved, while the viscous fluid strongly intumesces. On allowing the mixture to cool at this point, it solidifies to a tenacious stiff mass; on a farther application of heat, the disengagement of hydrosulphuric acid recommences and an oil of a garlic odour distils over. Stearic acid, when heated with sulphur, does not yield this volatile product, oleic acid, however, does so; in the distillation of the latter, or of almond-oil, with sulphur, the last portions that passed over contained margaric acid, which was not the case when oleic acid was distilled by itself; the formation of margaric acid was proved by the analysis of the substance itself, and of its combinations with protoxide of silver and oxide of ethyl. In order to obtain larger quantities of the oil which distilled over along with margaric acid, Anderson treated linseed-oil with sulphur in the following manner: the oil was heated with a little sulphur in a spacious retort until the reaction commenced, sulphur was then introduced in small doses into the mixture through a tube fixed in the retort, the fire being at the same time so regulated, that the liquid in the retort did not become too thick, by insufficient application of heat, or the reaction too violent, from the employment of too high a temperature. The oil, which passed over, commenced to boil at 71°, its boiling point rising continually. For the production of a purer substance, Anderson availed himself of the property possessed by this oil of forming precipi-

(1) Ann. Ch. Pharm. LXI, 362.

(2) Transact. of the Royal Soc. of Edinburgh, XVI, 363; Phil. Mag. [3] XXXI, 161; Ann. Ch. Pharm. LXIII, 370; J. Pr. Chem. XLII, 1; Ann. Ch. Phys. [3] XXI, 492; J. Pharm. [3] XII, 369 (in abstr.)

Action of sulphur and heat upon fatty oils.

tates with protochloride of mercury and bichloride of platinum.—The white precipitate, obtained by alcoholic solutions of the oil and of protochloride of mercury, was washed with ether and boiled with alcohol, in which it was somewhat soluble, being deposited from the hot, filtered solution, in the form of a white crystalline powder of nacreous lustre. The composition of this powder was found to be expressed by $C_{16} H_{16} S_5 Hg_4 Cl_2$; Anderson assigns to it the rational formula $(C_8 H_8 S_2 + Hg_2 Cl_2) + (C_8 H_8 S_2 + Hg_2 S)$, considering the compound $C_8 H_8$ (which he terms odmyl, from ὀδμή, odour) to be analogous with allyl. On submitting this mercury-compound, suspended in water, to a current of hydrosulphuric acid, it blackened, a peculiar odour was evolved, and, on subsequent distillation, an oil, floating on water, passed over, which, when dissolved in alcohol, yielded, with protochloride of mercury, a precipitate similar to that from which it had been obtained. Anderson considers this substance to be probably the bisulphide of odmyl, $C_8 H_8 S_2$.—The alcoholic solution of the first-mentioned oil yielded, with bichloride of platinum, a yellow precipitate, gradually increasing in quantity, the composition and properties of which, varied according as the more or less volatile portion of the oil had been employed in the preparation. The composition of the precipitate, obtained with the most volatile portion, corresponded approximately to the formula $C_{16} H_{16} S_5 Pt_2 Cl_2$ (the amounts of chlorine and sulphur were not determined).

Acids of Fir Resin.—In the first investigation of pinic and sylvic acids, the formula $C_{40} H_{32} O_4$ was assigned to them by H. Rose(1); sylvic acid was afterwards shown by H. Trommsdorff(2), and pinic acid by Liebig(3) to have the formula $C_{40} H_{30} O_4$, which was confirmed by Laurent(4). The latter chemist subsequently found(5) an acid, contained in the resin of *pinus maritima*, which he called pimaric acid, to be possessed of the same composition. He stated, that it was transformed, by distillation *in vacuo*, into another acid, pyromaric acid, without being altered in composition; and that, when left to itself, it changed to another isomeric modification, amorphous pimaric acid. The formula $MO, C_{40} H_{30} O_4$ has been assigned to the salts of these acids; this does not however agree with the views of

(1) Pogg. Ann. XXXIII, 33.
(2) Ann. Ch. Pharm. XIII, 169.
(3) Ann. Ch. Pharm. XIII, 174.
(4) Ann. Ch. Phys. [2] LXV, 324.
(5) Compt. Rend. IX, 797.

Laurent and Gerhardt; the former of whom endeavoured(1) to correct this formula, not so much by new analyses of the salts, as by ascertaining whether water is or is not liberated, in the combination of these acids with anhydrous bases. Silvic or pimaric acid, freshly fused and pulverized, yielded but little water when heated with protoxide of lead, but on adding ether to the mixture, and then drying at 140^0, water was disengaged in the proportion of 1 HO to 1 eq. of acid; for which reason Laurent has adopted the formula MO, $C_{40}\,H_{29}\,O_3$, for the salts of these acids. He likewise satisfied himself that pyromaric acid, formerly considered by him as a peculiar acid, is in fact identical with silvic acid; and observed that the resin which exudes from the *Pinus maritima*, after separation of the oil of turpentine by heat, is but a mixture of silvic and pimaric acids, and also that *crystallized* pimaric acid changes, in the course of time, into the amorphous or pinic acid, while the *fused* acid did not undergo any modification. In his investigation of pimaric acid, Laurent had assigned the name azomaric acid to the substance produced by the lengthened action of nitric acid on pimaric acid; on repeating his experiment (boiling, however, only seven or eight minutes with nitric acid, washing the product with water, dissolving it in alcohol and reprecipitating with water), he obtained a yellow amorphous, resinous substance, fusing with simultaneous decomposition, and having the same composition as azomaric acid; he has now adopted the formula $C_{40}\,H_{26}\,N_2\,O_{16}$ for this substance. The ammonia-salt of this acid is very soluble, and dries up to an orange-coloured mass. The salt of protoxide of lead, 2 PbO, $C_{40}\,H_{24}\,N_2\,O_{14}$, explodes feebly when heated. From this circumstance, and because the salts of this acid are of a yellow colour, Laurent assumes the nitrogen to exist in this substance as hyponitric acid, and its proper formula to be $C_{40}\,H_{26}$, 2 $(NO_4)\,O_8$.

Acids of the fir resin.

Researches on the Anacardium Fruit.—The kidney-shaped nut, known as the cashu-nut, or mahogany-nut, (*noix d'acajou*) descend-

(1) Ann. Ch. Phys. [3] XXII, 459; Ann. Ch. Pharm. LXVIII, 335; J. Pr. Chem. XLV, 61.—Strecker (Ann. Ch. Pharm. LXVIII, 338) believes that pimaric acid also might be identical with pyromaric or sylvic acid, since they are similar in nearly all their properties, the only differences, pointed out by Laurent, being that pyromaric gave, with acetate of protoxide of lead, a crystalline precipitate, while that formed by pimaric acid was amorphous, and that the acids, examined microscopically, had different crystalline forms. That the latter fact can be no reason for regarding pimaric acid as different from pyromaric or sylvic acid is evident, since pyromaric and sylvic acids were at first considered, by Laurent, as different, from the same circumstance, but are now recognized by him as identical.

Researches on the anacardium fruit.

ing from *Anacardium* or *Cassuvium occidentale*, contains, enclosed in its pericarp, a brown, balsamic substance, of a sharp, burning taste, and producing inflammation on the skin.

This balsamic substance has been accurately examined by Städeler(1). It is easily obtained, as a red-brown, almost inodorous liquid, resembling Peruvian balsam, by exhausting the crushed shells with ether, distilling off the latter from the clear extract and washing the resulting residue repeatedly with water, by which some tannic acid is removed. The product obtained amounts to about ⅛ the weight of the shells. It is easily soluble in alcohol and ether, the solutions reddening litmus-paper; it contains, besides a small quantity of ammonia and colouring substances which may be extracted by acids, two peculiar bodies: a fatty, crystallizable acid, *anacardic acid*, and an oily substance, called *cardole* (from *anacardium* and *oleum*), which produces inflammation and blisters on the skin.

Anacardic Acid.—Anacardic acid is separated from the cardole by digesting the alcoholic solution of the mixture with freshly precipitated hydrate of protoxide of lead, which retains the acid along with a product of decomposition, while cardole only remains in solution. The lead-compound, after washing with strong alcohol, is stirred up with water to a kind of milk, and digested with sulphide of ammonium. The resulting anacardate of ammonia is now decanted from the protosulphide of lead and decomposed with dilute sulphuric acid, which separates anacardic acid as a soft mass, solidifying in the cold. It is washed repeatedly with water and dissolved in alcohol; the moderately concentrated, coloured solution is then mixed with water, until it is rendered permanently turbid, upon which it is heated to ebullition, and tribasic acetate of protoxide of lead added, drop by drop, until the colouring matter, together with some anacardic acid is separated in dark, oleaginous drops. After the lapse of twelve hours, the clear fluid, having been poured off, is boiled for a short time with freshly precipitated carbonate of baryta; the resulting clear and colourless solution of anacardic acid is decanted after standing twelve hours, mixed with strong alcohol, and finally precipitated, at the boiling temperature, with an alcoholic solution of acetate of protoxide of lead. The white pulverulent anacardate of protoxide of lead, after being washed, is suspended in alcohol and decomposed by hydrosulphuric acid, or still better, by sulphuric acid; (unless alcohol be employed in the preparation of anacardate of lead, the

(1) Ann. Ch. Pharm. LXIII, 137; J. Pr. Chem. XLIII, 250 (in abstr.); Chem. Gaz. 1848, 29, 58; J. Pharm. [3] XIII, 457.

precipitate is formed in flakes, and is difficult to purify by washing). The alcohol being distilled off, anacardic acid separates, on addition of water, in an oleaginous state, becoming crystalline after the complete evaporation of the alcohol.—It is thus obtained as a white, crystalline, inodorous mass, of a feebly aromatic, and afterwards burning taste; it fuses at 26^0 and solidifies again only slowly; at 100^0, it has a peculiar odour and is decomposed at 200^0 into liquid products, that have not been farther examined. It produces oily stains on paper; it liquefies gradually in the air, emitting an odour of rancid fat. Its alcoholic and ethereal solutions redden litmus-paper. Anacardic acid.

Städeler found its composition to be expressed by the formula $C_{44} H_{32} O_7$. The analyses of the salts of baryta and protoxide of lead showed it to be bibasic, its true formula, therefore, being $2\,HO, C_{44} H_{30} O_5$.

Anacardic acid forms with bases, compounds, some of which are crystalline, others amorphous; the neutral salts contain 2 eqs. of base, and the acid salts 1 eq. of base and 1 eq. of water. Most of them are partially decomposed at 100^0. Städeler has examined the following: *anacardate of potassa* and of *ammonia;* these are amorphous, saponaceous, soluble in water and separable from their solutions by salts. The *acid potassa-salt* has the formula KO, HO, $C_{44} H_{30} O_5$.—*Anacardate of lime,* $2\,CaO, C_{44} H_{30} O_5 + 2\,HO$, and *anacardate of baryta,* $2\,BaO, C_{44} H_{30} O_5$, are white precipitates, becoming brown on desiccation.—*Anacardate of sesquioxide of iron,* $2\,Fe_2 O_3, 3\,C_{44} H_{30} O_5 + Fe_2 O_3, 3\,HO + 6\,HO$, is obtained, as a dark-brown, resinous precipitate, insoluble in water and alcohol, but soluble in ether, by mixing alcoholic solutions of sesquichloride of iron and of the acid, and adding ammonia, drop by drop. By neutralizing the acid with ammonia, salts more basic are obtained.—The *salts of protoxides of nickel* and *iron* are white, the *salt of protoxide of cobalt* is violet.—*Anacardate of protoxide of lead,* $2\,PbO, C_{44} H_{30} O_5$, is obtained by mixing hot alcoholic solutions of the acid and acetate of protoxide of lead, in the form of a white granular precipitate, becoming yellow and rancid in course of time. A double salt, anacardate and acetate of protoxide of lead, is formed upon mixing the alcoholic solution of this acid, containing cardole in admixture, first with water until turbidity ensues, and then with an alcoholic solution of acetate of protoxide of lead. It is amorphous, but, on being digested for a lengthened period with alcohol containing acetic acid, it is deposited in laminæ, resembling cholesterin. The analysis of this compound led to the formula, $PbO, C_4 H_3 O_3 +$

Anacardic acid. PbO, HO, C_{44} H_{30} O_5. It is insoluble in water; upon being boiled, it splits up into acetic acid and the neutral salt; ether dissolves out the acid salt, leaving the acetate of protoxide of lead.—*Anacardate of protoxide of silver*, AgO, HO, C_{44} H_{30} O_5, is a white pulverulent substance, soluble in alcohol, and decomposed at 130°.—By treating anacardic acid with nitric acid, it appears to yield the same products as other fatty acids, namely, suberic and butyric acids.

Cardole.—Cardole is contained, as above stated, in the liquid from which anacardic acid has been removed by hydrate of protoxide of lead. The solution contains, besides cardole, some of its products of oxidation, in combination with ammonia. In order to obtain this substance pure, the solution is boiled with a little hydrate of protoxide of lead, filtered, and the alcohol distilled off. The dark sherry-coloured residue is cardole, not perfectly pure. Its concentrated solution is now mixed with water until it becomes turbid, an aqueous solution of acetate of protoxide of lead is then added, upon which the mixture is heated to ebullition, and mixed with tribasic acetate of protoxide of lead, drop by drop, until the fluid has become almost colourless. The excess of lead is precipitated from the decolourized solution by sulphuric acid, a portion of the alcohol is removed by distillation, and the concentrated liquid mixed with water, upon which cardole separates. It is a yellow liquid, appearing of a reddish colour when in large quantities, and probably colourless when pure; when heated it acquires a slight and agreeable odour. Its spec. grav. is 0·978 at 23°. It is insoluble in water, easily soluble in alcohol and ether, non-volatile, inflammable, and absorbs oxygen slowly when exposed to the air, or more rapidly in the presence of tribasic acetate of protoxide of lead, becoming thereby dark. Its analysis leads to the formula C_{42} H_{31} O_4. —Cardole combines with bases, but has only a feeble affinity for them; those metallic oxides, which part with their oxygen easily, are reduced on forming compounds with it. Neutral acetate of protoxide of lead is not precipitated by cardole; basic salts of lead yield precipitates easily soluble in alcohol, and becoming rapidly flesh-coloured and then red-brown, when exposed to the air, in the moist state. A carefully prepared compound of this kind was found, by analysis, to agree with the formula PbO, C_4 H_3 O_3 + 3 PbO, C_{42} H_{31} O_4. Protoxide of lead is continually removed from this combination, by washing it with water.—By the action of nitric acid upon cardole, or of oxygen upon its solution in potassa, red products of oxidation are obtained, containing apparently different amounts of oxygen. The analysis of the lead-compound of one of these substances, produced by the continued action of air upon an alkaline solution

of cardole, gave, on analysis, numbers agreeing with the formula Cardole. $3\,PbO + 2\,C_{42}\,H_{30}\,O_7$. According to this, cardole would appear to have parted with 1 eq. of water, and assimilated an amount of oxygen equal to that it originally contained. The mixture of anacardic acid and cardole, extracted from the fruits of anacardium, owes its red colour to the presence of these products of oxidation, which are contained therein as ammonia-compounds; old and crippled fruit appears to yield more of these substances than the sound and vigorous specimens.

Städeler also brings cardole into notice as a medicinal agent; he states that it equals the expensive cantharadin in the rapidity of its action, and that the effect produced is of longer duration. For medicinal purposes, this substance is not required perfectly pure; it is only necessary, for its preparation, to exhaust the fruit, after removal of the kernels, with alcohol, to digest the extract with hydrate of protoxide of lead, until all acid reaction has disappeared; to remove the alcohol from the filtrate by distillation and to mix the residue with water in a cylindrical vessel, when the cardole will separate as an oily layer on the surface of the liquid.—On spreading a little cardole on the skin, f. i., of the chest, and covering the spot with some blotting-paper, a violent burning sensation will be felt, after from three to seven minutes; a white spot is first formed, and after from six to eight hours, a blister, which heals slowly and without any disagreeable consequences.

Uric Acid.—In a former investigation of uric acid and its compounds with bases, Bensch(1) showed that this acid is represented by the rational formula $HO, C_5\,H\,N_2\,O_2$, and that it forms neutral salts with potassa and soda, in which the water of hydration in the acid is replaced by 1 eq. of alkali; he determined, moreover, by accurate experiments the composition and the solubility of a series of acid urates. He has now continued this investigation in conjunction with J. Allan(2), and has succeeded in preparing also the neutral compounds of uric acid with the alkaline earths and likewise with protoxide of lead. We give here the results of these researches in a synoptical form ($\overline{U} = C_5\,H\,N_2\,O_2$).

(1) Ann. Ch. Pharm. LIV, 189. (2) Ibid. LXV, 181.

Uric acid.

Neutral potassa-salt	KO, $\bar{U}$
Acid potassa-salt	KO, 2 $\bar{U}$, HO
Neutr. soda-salt at 140°	NaO, $\bar{U}$
Acid soda-salt at 100°	NaO, 2 $\bar{U}$, 2 HO
" " " 170°	NaO, 2 $\bar{U}$, HO
Acid ammonia-salt	NH_4O, 2 $\bar{U}$, HO
Acid magnes.-salt at 100°	MgO, 2 $\bar{U}$, 7 HO
" " " 170°	MgO, 2 $\bar{U}$, 2 HO
Neutral lime-salt	CaO, $\bar{U}$
Acid lime-salt	CaO, 2 $\bar{U}$, 3 HO
Neutral strontia-salt	SrO, $\bar{U}$, 2 HO
Acid strontia-salt	SrO, 2 $\bar{U}$, 3 HO
Neutral baryta-salt	BaO, $\bar{U}$, HO
" " at 170°	BaO, $\bar{U}$
Acid baryta-salt	BaO, 2 $\bar{U}$, 3 HO
Neutr. lead-salt	PbO, $\bar{U}$
Acid lead-salt	PbO, 2 $\bar{U}$, 2 HO
Copper-salt dried over SO_3	3 CuO, 2 $\bar{U}$, 5 HO
" " at 140°	3 CuO, 2 $\bar{U}$, 2 HO

1 part of the following salts requires for solution as an average:

	Cold.	Boilg.
Uric acid	14500	1850
Neutral urate of potassa	44	35
Acid " " "	790	75
Neutral urate of soda	77	85
Acid " " "	1150	122
Acid urate of ammonia	1600	—
Neutral urate of baryta	7900	2700
Acid " "	insol.	insol.
Neutral urate of strontia	4300	1790
Acid " "	5300	2300
Neutral urate of lime	1500	1440
Acid " "	603	276
Acid urate of magnesia	3750	160

Neutral urate of potassa separates in fine crystalline needles when potassa, free from carbonic acid, is saturated in the cold with uric acid, and evaporated in a retort; it is caustic to the taste, attracts carbonic acid from the air, and is decomposed by boiling with water.—The corresponding *soda-salt* is obtained in hard warty crystals by a similar process.—The *acid potassa-* or *soda-salt* precipitates when carbonic acid is passed into a solution of uric acid in caustic alkali. Both are perfectly neutral, and do not absorb carbonic acid; their solutions are precipitated by chloride of ammonium and the bicarbonates of the alkalies, by salts of baryta, protoxide of lead and protoxide of silver.—*Neutral urate of ammonia* does not appear to exist; Bensch and Allan always obtained an acid salt, presenting itself sometimes in the form of a white, hard, amorphous mass, sometimes in fine needle-shaped crystals, which dried up to a light powder. By long boiling with water, which is frequently renewed, it is decomposed with loss of the whole of its ammonia. Dry uric acid does not increase in weight in an atmosphere of dry ammoniacal gas; if, however, the acid be evaporated with an excess of ammonia-solution it takes up just as much of the latter (100 parts of acid 10·17 ammonia) as corresponds to the acid salt.—The preparation of *neutral urate of magnesia*, as well as of double salts thereof with the ammonia-potassa- or soda-salt could not be effected, a mixture of the acid

salt with hydrate of magnesia being always obtained. *Acid urate of magnesia* separates after several hours in warty groups of satiny crystals, on mixing a hot saturated solution of the acid potassa-salt with sulphate of magnesia.—*Neutral urate of lime, baryta* and *strontia* may be readily obtained in a state of perfect purity by boiling the aqueous solutions of these bases with uric acid, or by mixing their soluble salts with neutral urate of potassa, with the precaution, however, of boiling the solution of the latter salt previously with a small quantity of the baryta- strontia- or lime-salt employed, and filtering off the resulting precipitate which consists chiefly of carbonate of the alkaline earth. These neutral urates are either crystallized in stellar groups of needles (strontia-salt), or they form opaque, granular masses devoid of crystalline structure (baryta- and lime-salt); they are not decomposed by water, their solutions have an alkaline reaction, and readily absorb carbonic acid from the atmosphere. The acid salts of the same bases are amorphous precipitates, which are formed by mixing acid urate of potassa with the soluble salts of the alkaline earths. —*Neutral urate of protoxide of lead* is obtained as a perfectly white, amorphous precipitate, insoluble in water and alcohol, by dropping a dilute solution of neutral urate of potassa into a likewise dilute boiling solution of nitrate of protoxide of lead, with the precaution of filtering off the yellow precipitate which is first formed. With acetate of lead a compound containing acetic acid is obtained.—The *acid urate of protoxide of lead* is a white, friable powder, insoluble in water, alcohol and ether. Its existence speaks much in favour of the bibasic nature of uric acid, whose true formula would then be $2\ HO, C_{10}\ N_4\ H_2\ O_4$.— The copper-salt, precipitated on mixing the acid potassa-salt with sulphate of protoxide of copper, is green and contains potassa, which is separated only on ebullition in the form of the acid salt; by boiling, the copper-salt turns brown, and by drying, violet.— Neutral urates with heavy metallic oxides other than protoxide of lead cannot be obtained pure; salts of protoxide of silver produce immediately a black precipitate with neutral urate of potassa.

Uric acid.

Decomposition of Uric Acid by Ferricyanide of Potassium and Potassa.—Schlieper(1) has published investigations upon the oxidation of uric acid by means of ferricyanide of potassium and potassa. To a lukewarm solution of uric acid in an amount of solu-

(1) Ann. Ch. Pharm. LXVII, 214; Chem. Gaz. 1849, 1.

Decomposition of uric acid by ferricyanide of potassium and potassa.

tion of potassa somewhat larger than necessary for the formation of neutral urate of potassa ($2\ KO, C_{10}\ N_4\ H_4\ O_6$), alternately ferricyanide of potassium (which is directly converted into ferrocyanide of potassium) and potassa, were gradually added until a complete decomposition of the uric acid was effected. Addition of potassa is necessary to reconvert the acid urate of potassa, which separates, into the neutral salt which is more soluble. The resulting alkaline liquid, smelling feebly of ammonia, and containing along with an excess of potassa, ferrocyanide of potassium and the product of decomposition of uric acid, was almost perfectly neutralized with sulphuric acid, (when much carbonic acid was evolved), and evaporated by boiling (when the odour of ammonia was constantly perceived). The greater part of the ferrocyanide of potassium being thus separated by crystallization, the remaining mother-liquor was farther evaporated, and treated with alcohol, by which ferrocyanide of potassium and sulphate of potassa were thrown down. The precipitated salt-mass, repeatedly boiled out with alcohol, yielded a solution from which crystalline crusts of an organic compound were separated on evaporation, a viscid potassa-syrup remaining behind, which even after long standing exhibited only traces of an indefinite crystalline appearance.—Another portion of uric acid was treated in a similar manner, with the difference only that the product was neutralized with acetic instead of sulphuric acid; after the greater portion of the ferrocyanide of potassium had been separated by crystallization, the remaining mother-liquor was precipitated with alcohol; the alcoholic filtrate in this instance gave no crystals, but only the viscid syrup, from which the acetate of potassa which it contained was removed by treatment with absolute alcohol. The residuary salt-mass, insoluble in alcohol, was now dissolved in water, the solution heated, and the ferrocyanide of potassium precipitated by a slight excess of acetate of copper; in the filtered solution a precipitate of neutral oxalate of potassa was produced on addition of alcohol.—The above-mentioned crystalline organic compound, after having been purified by recrystallization from water, was found to be allantoïn both by its reactions and by analysis.—The viscid syrup readily dissolved in water, and was reprecipitated from this solution by absolute alcohol, in the form of white flakes, which, after separation from the liquid, quickly deliquesced when exposed to the air. The aqueous solution was treated with acetate of protoxide of lead, and the resulting oxalate filtered off, when upon addition of ammonia free from carbonic acid, a white, curdy, lead-compound

was thrown down, containing variable proportions of lead, in which (when dried at 100⁰), an organic compound is present, having the composition $C_6 N_2 H_4 O_6$. To this substance Schlieper gives the name, *lantanuric acid.* If the syrup be dissolved in a small amount of water, sufficient spirit of wine being added to cause a slight turbidity which is again redissolved on addition of a few drops of water, crystalline crusts are very slowly separated from this liquid, which ceases to have an acid reaction; when purified by re-crystallization, they were found to be acid lantanurate of potassa, $KO, C_6 N_2 H_4 O_6 + HO, C_6 N_2 H_4 O_6 + 4 HO$, (4 HO are evolved at 100⁰). Lantanurate of protoxide of silver appears to be decomposed by drying at 100⁰, 3 HO being evolved from the acid; the salt becomes converted into $AgO, C_6 N_2 H O_3$.

Decomposition of uric acid by ferricyanide of potassium and potassa.

Schlieper considers alantoin and carbonic acid as the essential products of decomposition of uric acid when treated with ferricyanide of potassium and potassa. 2 equivs. of uric acid ($C_{10} N_4 H_4 O_4$), 2 equivs. of ferricyanide of potassium, 4 equivs. of potassa, and 2 equivs. of water, yield 4 equivs. of ferrocyanide of potassium, 2 equivs. of carbonate of potassa and 2 equivs. of allantoin. Urea, which he once found in small quantity among the products of decomposition, and a red body adhering strongly to the allantoin, he considers as secondary products.

If allantoin be allowed to remain some time (one or two days) dissolved in concentrated potassa, it ceases to be precipitated by acids; when boiled, the solution yields only a very small quantity of ammonia and no trace of oxalic acid. 2 equivs. of allantoin have assimilated 2 equivs of water, and become converted into an acid, *hidantoic acid.* The alkaline solution, when treated with acetic acid until it assumes an acid reaction, and subsequently with alcohol, becomes milky, hidantoate of potassa being separated as a colourless oily fluid; this salt could not be obtained in the crystalline state.—The liquid supersaturated, as above mentioned, with acetic acid, yields with acetate of protoxide of lead, after a short time, a white precipitate, having, when dried at 100⁰, the composition $PbO, C_8 N_4 H_8 O_8$. The acid separated from the lead-salt by hydrosulphuric acid, was likewise uncrystallizable; it could be obtained only in the form of a syrup, which, on addition of alcohol, is converted to a white, friable, readily deliquescent mass; the evaporated acid, when treated with cold potassa-solution, evolves ammonia; it yields no precipitate with baryta- and lime-water, but upon addition of alcohol, thick white flakes are separated; when neutralized with ammonia, it gives with chloride of barium a white

Hippuric acid.

precipitate; hidantoic acid does not expel carbonic acid from carbonate of soda; on heating a solution of the acid in ammonia, the latter is evolved on evaporation in the water-bath; hence the acid is decomposed during evaporation, as was afterwards confirmed by the analysis of a silver-salt prepared with such an acid (which contained 2 Ag to 5 N).

Hippuric Acid.—For the rapid preparation of hippuric acid, Gregory(1) recommends to treat fresh urine of horses or cows with an excess of milk of lime, to strain, after a few moments' ebullition, the hot liquid, to reduce by boiling the clear solution of hippurates as quickly as possible to from $\frac{1}{8}$ to $\frac{1}{10}$ (according to the concentration of the urine) of its original volume, and to supersaturate with hydrochloric acid; after cooling, a considerable crystallization of reddish or yellowish hippuric acid is obtained. (Experiments made in the Giessen laboratory have proved this process to be very excellent).

According to Strecker(2), a solution of hippuric acid in concentrated nitric acid, when treated with binoxide of nitrogen, evolves nitrogen, the acid $C_{18}\ H_8\ O_8$ being obtained, of which hippuric acid may be considered to be the amidogen-compound. The acid thus prepared, containing no nitrogen, dissolves readily in ether; the baryta-salt crystallizes in satiny needles, readily soluble in water; the silver-salt, AgO, $C_{18}\ H_7\ O_7$, dissolves pretty freely in boiling water and crystallizes, on cooling, in fine needles; when subjected to the action of heat, it evolves oil of bitter almonds.

Amides, Nitriles, Anilides, and Collateral Matters.—We here arrange, in a separate chapter, a class of compounds which may be considered as derived from ammonia, or organic bases, by the elimination of water. Thus, the amides (salts of oxide of ammonium — 2 HO), and the nitriles (salts of oxide of ammonium — 4 HO), are derived from ammonia-compounds; corresponding derivatives have been obtained from aniline and naphthalidine.

Amides: Phosphamide.—Incidentally to H. Rose's investigation of a compound of phosphorus with nitrogen, Liebig and Wöhler(3) published some observations upon the products of the action of

(1) Chem. Soc. Mem. III, 330; Phil. Mag. [3] XXXI, 127; Ann. Ch. Pharm. LXIII, 125; J. Pr. Chem. XLII, 40.
(2) Ann. Ch. Pharm. LXVIII, 54.
(3) Ibid. XI, 139.

ammonia-gas on pentachloride of phosphorus as the results of a fragmentary investigation, which, without claiming any degree of accuracy, were nevertheless calculated to afford some assistance to future inquirers. They found that one of the products thus obtained, when treated with water, yielded as residue an insoluble body, whose composition is expressed by the formula $P N_2 H_2 O_2$, and that, together with this compound, another product, of the appearance of camphor, was always produced.—Gerhardt(1) regards the product, which is insoluble in water, as $P N_2 H_3 O_2$ (which formula, excepting hydrogen, requires almost exactly the same percentage as Liebig and Wöhler's formula $P N_2 H_2 O_2$), *i. e.*, as a compound which stands in a similar relation to phosphate of ammonia as do the amides to the salts of ammonia ($2 NH_4 O, HO, PO_5 - 6 HO = P N_2 H_3 O_2$); and hence the name which he proposes, *phosphamide*. The formation of the camphor-like body is not explained by Gerhardt's mode of viewing; he considers its production as accidental and immaterial.—In support of his view, Gerhardt(2) adduces that, the body which he regards as phosphamide, completely dissolves in dilute sulphuric acid when gently heated, without evolution of gas, and that the thick syrupy solution yields crystals of bisulphate of ammonia, while the mother-liquor contains phosphoric acid. Phosphamide.

Sulphocarbamide.—If bisulphide of carbon be placed in contact with a large mass of ammonia-gas, the bottom of the vessel, according to Laurent(3), will be covered, within twenty-four hours, with a yellow deposit, which, when observed under the microscope, is resolved into a mixture of crystalline needles, and a yellow amorphous substance. By the action of heat, this mixture evolves hydrosulphuric acid and several other substances; when dissolved in water and treated with hydrochloric acid, to expel the hydrosulphuric acid, it assumes a blood-red colour with sesquichloride of iron. Laurent concludes, that bisulphide of carbon gives with ammonia hydrosulphuric acid and sulphocarbamide, identical with hydrosulphocyanic acid ($2 CS_2 + NH_3 = 2 HS + C_2 N S_2 H$); the hydrosulphocyanic acid yields with ammonia, sulphocyanide of ammonium, while hydrosulphuric acid combines either with ammonia or with bisulphide of carbon and ammonia, to form hydrothiocarbonate of ammonia (sulphocarbonate of ammonia).

(1) Ann. Ch. Phys. [3] XVIII, 188; comp. Berzelius' Jahresber. XXVII, 44.
(2) Ibid. XX, 255; J. Pharm. [3] XI, 457.
(3) Ibid. XXII, 103; J. Pr. Chem. XLIV, 162.

Metacetamide, Acetamide, Valeramide.

Metacetamide, Acetamide, Valeramide.—Dumas, Malaguti and Leblanc(1) found, that metacetonate of oxide of ethyl, in contact with liquid ammonia, is quickly converted into *metacetamide*. *Acetamide*, $C_4 H_5 N O_2$, was obtained in a similar manner from acetic ether: it is solid, white, crystalline, and deliquescent, fusible at 78°, and yields, on cooling, beautiful crystals; it boils at 221°. *Valeramide* is prepared in the same manner as butyramide(2). They find that the amides of the acids $C_n H_n O_4$, when acted upon by potassium at a gentle heat, give rise to an evolution of gas and to the formation of cyanide of potassium. With regard to this reaction, they remark that these amides, $C_n H_{n+1} O_2 N$, may be viewed as consisting of hydrocyanic acid, H, $C_2 N$, and an alcohol, $C_{n-2} H_n O_2$; they did not succeed, however, in proving the pre-existence, f. i., of pyroxylic spirit in acetamide. The amides of other acids, f. i., benzamide and cuminamide, yield no cyanide of potassium when treated with potassium at their fusing temperature. The formation of cyanide of potassium in the decomposition of benzamide by means of potassium, as observed by Liebig and Wöhler, they consider as the result of a secondary reaction.—At a later period(3), they communicated the fact that the conversion of ethers into amides, which in many cases is extremely slow, when taking place at the common temperature, may be remarkably accelerated by performing the experiment in sealed tubes, at a temperature higher than 100°.

Chlorocarbethamide, Chloracetamide. — According to Gerhardt(4), chlorocarbethamide, produced by the action of ammonia upon chlorinated carbonic ether, whose composition, according to Malaguti's(5) investigation, is represented by the formula $C_{10} H_6 Cl_7 N_3 O_3$, is, in all its properties (the composition, however, was not examined), identical with chloracetamide; he states that the former likewise has the composition $C_4 H_2 Cl_3 N O_2$. Malaguti's

(1) Compt. Rend. XXV, 656.

(2) Dessaignes and Chautard communicate, that in a mixture of valerianic ether with seven or eight times its volume of concentrated solution of ammonia, which was frequently agitated, the ether disappeared after four summer-months. By evaporation at a gentle heat, valeramide, $C_{10} H_{11} N O_2$, was obtained in long, delicate, brilliant, crystalline plates. Valeramide, according to their statements, is readily soluble in water, fusible above 100°, subliming almost completely at the same temperature; only by boiling with caustic potassa, is ammonia evolved from it. (J. Pharm. [3] XIII, 244; J. Pr. Chem. XLV, 48; Ann. Ch. Pharm. LXVIII, 333.)—A. W. Hofmann obtained valeramide in the same manner (Ann. Ch. Pharm. LXV, 56).

(3) Compt. Rend. XXV, 734.

(4) Ibid. XXII, 116; J. Pharm. [3] XIV, 233.

(5) Comp. Berzelius' Jahresber. XXVI, 760.

Chlorocarbethamide Chloracetamide.

chlorocarbethamate of ammonia, for which he found the composition, $NH_4O, C_{10}H_9Cl_7N_2O_8$, according to Gerhardt, is $NH_4O, C_4Cl_3O_3$, chloracetate of ammonia.—Malaguti(1) admits that chlorocarbethamide, prepared by means of aqueous ammonia, is identical with chloracetamide, but not the substance obtained by ammoniacal gas, whose composition, however, might be represented by the formula, $C_{10}H_6Cl_7N_3O_4$. Malaguti states that he also found that the product obtained by the action of ammonia upon chlorinated oxalic ether, and named chloroxethamide, is likewise chloracetamide, and expresses the opinion, that although all compound ethers whose hydrogen is entirely replaced by chlorine, when treated with aqueous ammonia, will probably yield chloracetamide, some of them, when acted upon by anhydrous ammonia, give rise to the formation of other products.—Gerhardt(2) has now found that chlorocarbethamide, even when obtained by anhydrous ammonia, has the same properties as chloracetamide.

Anisamide.—According to Cahours(3), chloride of anisyl (p. 413), when in contact with ammonia-gas, evolves much heat, and yields *anisamide*, which crystallizes from alcohol in beautiful prisms. It is likewise obtained by the treatment of anisic ether with ammonia. Its composition is $C_{16}H_9NO_4$.

Cuminamide.—According to Field(4), a solution of cuminic acid in strong liquid ammonia, when evaporated to dryness and heated, evolves ammonia, while cuminic acid sublimes, another portion of the salt being converted, with separation of water, into a white crystalline body, difficultly soluble in water, and subsequently into an oil (cumonitrile, comp. p. 458), which has a very powerful odour, (by experience only, the temperature can be so regulated as to produce the one or the other of these two bodies). The white crystalline body is *cuminamide*, $C_{20}H_{13}NO_2 = NH_4O, C_{20}H_{11}O_3 - 2HO$. It may be likewise obtained by gradually heating cuminate of ammonia in a strong, sealed, glass tube, in an oil-bath, to near the boiling-point of the oil; when cold, the mass is solid and crystalline, insoluble in cold water and ammonia, but very soluble in hot water, from which solution it crystallizes on cooling. By recrystallization from hot water (to which some ammonia is added,

(1) Compt. Rend. XXVII, 188; J. Pharm. [3] XIV, 289.
(2) Ibid. XXVII, 238; J. Pharm. [3] XIV, 291.
(3) Loc. cit. p. 452.
(4) Chem. Soc. Mem. III, 404; Phil. Mag. [3] XXXI, 459; Ann. Ch. Pharm. LXV, 45; J. Pr. Chem. XLIV, 136; J. Pharm. [3] XIII, 225.

Cuminamide. in order to remove traces of cuminic acid which may be present) cuminamide, when rapidly separated from a concentrated solution, is obtained in brilliant, white, tubular crystals, similar to those of benzamide; when crystallized slowly from a dilute solution, it presents the form of long, opaque needles. It is soluble in every proportion in cold and warm alcohol, and is decomposed only with difficulty, by long ebullition with mineral acids, or strong potassa-solution, like the amides in general.

Nitrobenzamide.—By long fusion of nitrobenzoate of ammonia, Field obtained a substance, insoluble in cold water and ammonia, but crystallizing from its solution in hot water, in beautiful yellow needles, which was found to be *nitrobenzamide*, $C_{14} H_6 (NO_4) NO_2$. The fusion must be conducted with great care, for nitrobenzoate of ammonia readily explodes when strongly heated.

Chlorobenzamide.—A chlorobenzoic acid, of uncertain composition, containing either, $HO, C_{14} H_3 Cl_2 O_3$, or $HO, C_{14} H_2 Cl_3 O_3$, when converted into an ammonia-salt, and then treated in the manner above-mentioned, yielded to Field a product insoluble in cold water and ammonia, and crystallizing from the hot aqueous solution in long needles; chlorobenzoic acid, $HO, C_{14} H_4 Cl O_3$, prepared on purpose, when combined with ammonia and heated, blackened, with separation of carbon.

On chloroniceamide, comp. p. 407.

Phtalamic Acid.—According to Marignac(1), anhydrous phtalic acid ($C_{16} H_4 O_6$), when acted upon by ammonia is converted into phtalamide ($C_{16} H_6 NO_5$). Respecting this reaction, Laurent(2) makes the following observations. If anhydrous phtalic acid be dissolved in hot alcohol, and then treated with ammonia, small, colourless prisms separate on cooling, whose ends are terminated by two planes; they are readily soluble in water, when dissolved in a small portion of that solvent, mixed with alcohol, and subsequently with bichloride of platinum, a precipitate of bichloride of platinum and ammonium is formed immediately; the filtered solution, when boiled with excess of bichloride of platinum, yields an additional precipitate of the platinum-salt. The above-mentioned crystals are the ammonia-salt of a new acid, *phtalamic acid*, and have the composition, $NH_4 O, C_{16} H_6 NO_5$; the first precipitate produced by bichloride of platinum, contains the ammonia of the salt, and only upon ebullition the nitrogen of the acid is

(1) Ann. Ch. Pharm. XLII, 215; Berzelius' Jahresber. XXIII, 542.
(2) Ann. Ch. Phys. [3] XXIII, 117; J. Pr. Chem. XLV, 174.

likewise separated in the form of the ammonium double compound. If phtalamate of ammonia be precipitated with acetate of protoxide of lead, and the precipitate decomposed by hydrosulphuric acid, the liquid, when evaporated, yields crystals of biphtalamate of ammonia; hence, phtalamic acid, $C_{16} H_7 N O_6$, absorbs, during evaporation, 2 equivs. of water. By addition of a concentrated solution of nitrate of protoxide of silver to a boiling alcoholic solution of phtalamate of ammonia, a large quantity of fine needles of phtalamate of protoxide of silver, $AgO, C_{16} H_6 NO_5$, are formed, after some minutes; by boiling water these crystals are decomposed with formation of brilliant plates, which Laurent considers to be phtalamide silver-ammonium $C_{16} H_4 \left(\begin{smallmatrix} Ag \\ H_3 \end{smallmatrix} N\right) N O_4$. If nitrate of silver be added to a boiling alcoholic solution of phtalamide, no precipitate is formed; but after addition of ammonia a precipitate is produced, sometimes crystallizing in plates, and sometimes in the form of a powder; this latter compound Laurent believes to be phtalimide-silver ($C_{16} H_4 Ag N O_4$. Phtalamic acid.

Action of Hydrosulphuric Acid on Hydramides.—The experiments of Liebig and Wöhler upon the action of hydrosulphuric acid on aldehyde-ammonia (comp. thialdine) induced Cahours(1) to investigate the deportment of this acid with the class of compounds designated by Gerhardt, as hydramides.—If a current of hydrosulphuric acid be passed through an alcoholic solution of hydrobenzamide, the liquid becomes rapidly turbid, a perfect decomposition taking place if an excess of hydrosulphuric acid be employed; no sulphur, however, is deposited. The liquid when allowed to stand for some time becomes clear, and contains sulphide of ammonium; the precipitate which deposits, when washed with alcohol, forms a white farinaceous powder, which is Laurent's hydrosulphobenzoyl [$C_{42} H_{18} N_2 + 8 HS = 3 (C_{14} H_6 S_2) + 2 NH_4 S$].—When treated in a similar manner, hydrocinnamide yields a product $C_{18} H_8 S_2$ (Cahours terms it *thiocinnole*), and the compound $C_{16} H_8 S_2 O_2$ hydranisamide (thianisole). Both have the same appearance as the substance obtained from hydrobenzamide.—Fownes' furfuramide $C_{30} H_{12} N_2 O_6$, yields with hydrosulphuric acid a yellowish powder $C_{10} H_4 S_2 O_2$, which Cahours, referring to its analogy with furfurole ($C_{10} H_4 O_4$), has designated *thiofurfole*.—Hydrosalamide, in alcoholic solution, when treated with hydrosulphuric acid is converted into a similar powder, imparting a violet-red

(1) Compt. Rend. XXV, 457.

Action of hydrosulphuric acid on hydramides.

colour to salts of sesquioxide of iron; it is capable of combining with the alkalies, in the same manner as hydride of salicyl (salicylous acid); and contains a large quantity of sulphur. Cahours believes that it is the latter compound, in which half the oxygen is replaced by sulphur, $C_{14}\ H_6\ S_2\ O_2$.—Cahours recalls the fact, that Laurent pointed out the formation of hydrosulphobenzoyl by the action of sulphide of ammonium upon an alcoholic solution of oil of bitter almonds; he himself shows, that thiocinnole and thianisole may be formed likewise by acting with sulphide of ammonium upon an alcoholic solution of cinnamon oil and hydride of anisyl. By similar treatment of cumin oil a resinous body containing sulphur is obtained which is difficult to purify, and whose composition approximately corresponds to the formula $C_{20}\ H_{12}\ S_2$.

Nitriles.—Frankland and Kolbe(1) regard the class of bodies designated by the name nitriles, as cyanogen-compounds (benzonitrile $C_{14}\ H_5\ N$, f. i., as cyanide of phenyl $C_{12}\ H_5\ Cy$), in which the cyanogen, just as chlorine in chloride of ethyl, cannot be ascertained by the usual reagents. They endeavour to support their view by pointing out that the boiling points of valeronitrile ($C_{10}\ H_9\ N$; 125^0), and cyanide of amyl ($C_{12}\ H_{11}\ N$; 146^0) differ by the number of degrees, characteristic of analogous substances exhibiting a difference of $C_2\ H_2$ in their composition, and that hydrated metacetonic acid and cyanide of ethyl, hydrated valerianic acid and valeronitrile, hydrated caproic acid and cyanide of amyl, and, lastly, hydrated benzoic acid and benzonitrile show nearly the same difference in their boiling-points.

Acetonitrile.—Dumas(2) has arrived at the same view. He found that by the action of anhydrous phosphoric acid upon crystallized acetate of ammonia, a liquid passed over on distillation, which, by digestion with a saturated solution of chloride of calcium and rectification over fused chloride of calcium and magnesia, is obtained in a state of perfect purity; it boils at 77^0, and is miscible with water in all proportions. Its composition is $C_4\ H_3\ N$ (*acetonitrile*, acetate of oxide of ammonium — 4 equivs. of water); 1 equiv. of this substance in the state of vapour occupies 4 vols.; by its reactions it may be regarded as cyanide of methyl ($C_2\ H_3$, $C_2\ N$). When boiled with a solution of potassa, this compound evolves ammonia, acetic acid being reproduced; chromic acid and boiling nitric acid have no action upon it. Potassium, even in the cold, acts very violently upon it,

(1) Loc. cit. p. 418. (2) Compt. Rend. XXV, 383.

heat being evolved, while cyanide of potassium is produced, and an inflammable gaseous mixture, consisting of carburetted hydrogen, and free hydrogen is disengaged. Dumas mentions that benzonitrile, discovered by Fehling, arising from benzoate of oxide of ammonium, likewise by the loss of 4 equivs. of water, may also be prepared by distillating the benzoate with anhydrous phosphoric acid. Dumas considered it probable, that the ammonia-compounds of volatile acids $NH_4O, C_n H_{n-1} O_3$ generally might give rise to the formation of ethereal cyanides $C_{n-2} H_{n-1} O, C_2N$ from which the alcohols $C_{n-2} H_n O_2$ might be prepared (n representing invariably an even number). Aceto-nitrile.

Chloracetonitrile.—Dumas has pursued this investigation in conjunction with Malaguti and Leblanc. They found(1), in the first place, that chloracetate of oxide of ammonium, $NH_4 O, C_4 Cl_3 O_3$, in an analogous manner, yields a liquid compound $C_4 Cl_3 N$ (*chloracetonitrile*), which has a spec. grav. of 1·444, boils at 81°, and in the state of vapour exhibits a condensation to 4 vols; with potassa it regenerates choracetic acid; it is also produced by the action of anhydrous phosphoric acid upon chloracetamide. Butyrate and valerianate of oxide of ammonium, by losing 4 equivs. of water, are converted in the same manner into analogous compounds, which, when treated with hydrate of potassa, again yield the original acids. The action of potassium gives rise to the formation of cyanide of potassium, and a mixture of hydrogen with a carbohydrogen, the condensation of which increases with the value of n in the formula of the acid employed (the acids being generally represented by $C_n H_n O_4$). They point out that the conversion of oxalate and formiate of oxide of ammonium into cyanogen and hydrocyanic acid (in both instances by elimination of 4 equivs. of water) are absolutely analogous cases.—Moreover(2), they have proved, that acetonitrile and cyanide of methyl are identical (*see* p. 421), and, that the ethereal cyanogen-compounds $C_n H_{n+1}, C_2 N$ when treated with hydrate of potassa, are decomposed not in the same manner as the other compound ethers, with formation of an alcohol ($C_n H_{n+2}O_2$); but, with production of an acid $C_{n+2} H_{n+2}O_4$ and evolution of ammonia. They state, in addition, that butyramide and benzamide, similarly to the corresponding ammonia-salts, are likewise converted into nitriles by the action of anhydrous phosphoric acid, and that benzonitrile exhibits with potassium a deportment differing from that of the nitriles of the acids $C_n H_n O_4$,

(1) Compt. Rend. XXV, 442.  (2) Ibid. XXV, 473.

Butyronitrile and Valeronitrile.

inasmuch as neither any cyanide is formed, nor gas evolved.—Lastly, they have shown the conversion of acetamide, metacetamide, butyramide, and valeramide into the corresponding nitriles, by the action of anhydrous phosphoric acid(1).

Butyronitrile and Valeronitrile.—*Butyronitrile* ($C_8 H_7 N$), or cyanide of metacetyl ($C_6 H_7, C_2 N$) is an oily liquid of an agreeable odour, reminding one of bitter-almond-oil, of a spec. grav. 0·795 at 12·5^0 and a boiling-point of 118·°5; with potassium it yields cyanide of potassium, hydrogen and a new carbohydrogen. Valeronitrile ($C_{10} H_9 N$), or cyanide of butyryl ($C_8 H_9, C_2 N$) is identical with the substance first described by Schlieper under the former name, and comports itself with potassium similarly to the preceding compounds (comp. also "Decomposition of casein, &c., by sulphuric acid and bichromate of potassa").

According to A. W. Hofmann(2) nitriles are not formed on distillation of acetate, butyrate, or valerianate of ammonia. He obtained, however, butyronitrile and valeronitrile by passing the vapour of butyramide and of valeramide through a red-hot tube filled with lime. The formation of nitriles by this method, according to Hofmann, succeeds only with difficulty, and he believes that Dumas' method of preparation by means of anhydrous phosphoric acid is preferable.—Laurent and Chancel(3) have likewise found, that by passing the vapour of butyramide ($C_8 H_9 NO_2$) over caustic baryta heated to dull redness, a transparent colourless liquid is obtained, which is *butyronitrile* $C_8 H_7 N$. They consider this method of preparing the nitriles in many cases more advantageous than the former. Benzoate of ammonia when treated in this manner gave only benzole.

Cumonitrile.—If cuminate of ammonia be heated to fusion, and the melted mass retained in a state of lively ebullition, according to Field(4), a yellowish oil distils over with water; as soon as the distillation of the oil slackens, it is separated from the aqueous distillate, the latter returned to the residue in the retort, distilled again, and the process repeated several times. The oil thus obtained is first washed with ammonia, then with hydrochloric acid, and lastly with water; it is then rectified with chloride of calcium. The distillate collected in the middle of the process,

(1) Compt. Rend. XXV, 656. (2) Ann. Ch. Pharm. LXV, 55.
(3) Compt. Rend. XXV, 884; J. Pharm. [3] XIII, 464; Ann. Ch. Pharm. LXIV, 332.
(4) Loc. cit. p. 453.

when heated in contact with platinum wire, exhibited the boiling-point 239^0 at $758{\cdot}5^{mm}$ bar.; it is *cumonitrile*, $C_{20} H_{11} N = NH_4 O$, $C_{20} H_{11} O_3 - 4 HO$, a colourless liquid, powerfully refracting light, of a strong agreeable odour, and burning taste, which is somewhat soluble in water, and mixes in all proportions with alcohol and ether. It has a spec. grav. 0·765 at 14^0; its vapour burns with a luminous flame, and deposits a large quantity of carbon. Strong nitric acid acts but slowly upon it; when boiled with it, crystals of cuminic acid separate after several days. When heated with potassium, the colour of cumonitrile is darkened, another oily compound being formed; upon treating the mass with water, and applying the ordinary test for cyanogen, a copious precipitate of Prussian blue was obtained. An alcoholic solution of potassa does not immediately act upon cumonitrile, but after one or two days the liquid becomes solid, a crystalline mass being produced which is a mixture of cuminamide and cumonitrile. Cumonitrile.

Action of Hydrosulphuric Acid upon Benzonitrile.—On saturating, according to Cahours(1), an alcoholic solution of benzonitrile, containing some ammonia, with hydrosulphuric acid, evaporating the yellowish-brown liquid to ¼th, and adding water, sulphur-yellow flakes are separated, crystallizing from their hot aqueous solution in long satiny needles. They are $C_{14} H_7 N S_2$, or benzamide in which the oxygen is replaced by sulphur. When treated with protoxide of mercury, water, protosulphide of mercury and benzonitrile are formed; potassium decomposes it with formation of sulphide and cyanide of potassium(2).

Anilides.—In 1846 Gerhardt pointed out, that oxygen and hydrogen in the same proportion as in water may be eliminated from aniline-salts, a class of compounds being produced analogous to

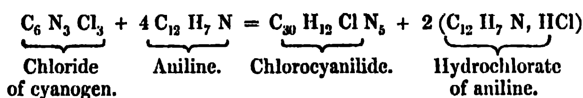
(1) Compt. Rend. XXVII, 239; J. Pr. Chem. XLV, 354.

(2) Incidentally to these experiments, Cahours discusses the deportment of hydrosulphuric acid with nitrogenized substances generally.—In many cases sulphur is precipitated, while the compound treated simply assumes hydrogen (alloxan, indigo-blue).—Or the separation of sulphur is attended by assimilation of hydrogen, and elimination of water (formation of organic bases, and amidogen-acids, by the action of hydrosulphuric acid on neutral or acid substitution-products, containing NO_4 instead of H).—In other cases, along with water, nitrogen is separated in the form of sulphide of ammonium, while organic bases, containing sulphur, are formed (thialdine).—Or the whole of the nitrogen is converted into sulphide of ammonium, while neutral sulphur-bodies are generated (action of hydrosulphuric acid upon hydramides).—Or lastly, hydrosulphuric acid is directly absorbed, compounds being formed, which correspond in their composition to the amides (action of hydrosulphuric acids upon the nitriles).

Chloro-cyanilide.

the amides, and which has been designated by the name anilides. Researches upon these compounds have been published during 1847 and 1848, by Laurent, and jointly with him by Gerhardt.

Chlorocyanilide.—Laurent(1) found, that by treating powdered solid chloride of cyanogen with aniline, in the presence of some warm water, and so much alcohol as is necessary to dissolve the aniline, a white precipitate of *chlorocyanilide* is immediately formed, insoluble in water, and crystallizing from hot alcohol in brilliant plates. Its composition is $C_{30}\ H_{12}\ Cl\ O_5$.



$$\underbrace{C_6\ N_3\ Cl_3}_{\text{Chloride of cyanogen.}} + 4\underbrace{C_{12}\ H_7\ N}_{\text{Aniline.}} = \underbrace{C_{30}\ H_{12}\ Cl\ N_5}_{\text{Chlorocyanilide.}} + 2\underbrace{(C_{12}\ H_7\ N,\ HCl)}_{\text{Hydrochlorate of aniline.}}$$

Hence its formation is similar to that of chlorocyanamide. Chlorocyanilide is not volatile without the action of heat, it liquifies, and solidifies on cooling to a crystalline mass; when heated more strongly, it loses 11·8 per cent of hydrochloric acid becoming gradually less liquid, vesicular, and solidifying ultimately to a mass presenting an appearance similar to that of dried albumin. Laurent considers this transparent, greenish residue, to be $C_{30}\ H_{11}\ N_5$ (the formation of this compound presupposes the evolution of 12·2 per cent of hydrochloric acid). Chlorocyanilide dissolves slowly in boiling potassa; from the solution nitric acid precipitates a white flaky body, insoluble in ammonia, but soluble in hot dilute nitric acid, and separating from this solution on cooling in the form of a jelly. Laurent considers this body as $C_{30}\ H_{13}\ N_5\ O_2$ (analysis, however, gave 2 per cent of carbon less than this formula requires,) and believes that its formation is analogous to that of chlorocyanamide.

Fluosilicanilide.—Laurent farther states, that according to experiments made by himself and Delbos, aniline absorbs terfluoride of silicium (59·5 aniline absorb 40·5 of gas), a slightly yellowish mass being produced, which, exhausted by boiling spirit, pressed and dried at 100°, may be sublimed by a slow heat, as a light white crust. This sublimate was found to contain 39·5 per cent of carbon, and 4·4 per cent of hydrogen; when mixed with protoxide of lead, moistened and heated, and strongly ignited, after addition of a few drops of nitric acid, 1 part of sublimate caused an increase of 0·422 in the weight of the protoxide of lead. Laurent considers this sublimate as *fluosilicanilide*, $C_{48}\ H_{33}\ N_4\ Fl_{11}\ Si_4\ O_6$; he believes, that

(1) Ann. Ch. Phys. [3] XXII, 97; J. Pr. Chem. XLIV, 157.

it forms with the co-operation of the water of the aqueous spirit, with which the direct product of the reaction was treated; he remarks, however, himself, that the product sublimes also before treatment with spirits of wine, when, in his opinion, it is not as yet converted into fluosilicanilide. This compound is slightly soluble in boiling alcohol, from which it is deposited in small very brilliant plates. Fluosilic anilide.

The rest of Laurent's paper is devoted to considerations of the constitution and the chemical character of this and similar compounds, and to proposals of an appropriate nomenclature.

Investigations made by Gerhardt and Laurent(1) of the anilides, have led to the following results.

Oxanilide.—Oxanilide(2), the compound corresponding to oxamide, had been previously prepared by Gerhardt.

Oxanilic Acid.—Gerhardt and Laurent now endeavoured to form *oxanilic acid*, the compound corresponding to oxamic acid. This succeeds easily by fusing aniline with a large excess of oxalic acid, and heating the mixture strongly for eight or ten minutes; on boiling the mass with water, and filtering, coloured crystals of oxanilate of aniline are deposited from the filtrate, while oxanilide remains on the filter; the mother-liquor contains an excess of oxalic acid, a certain amount of oxanilic acid, or oxanilate of aniline, and some formanilide. The crystals which have been first deposited are brown, and retain this colour even after two or three recrystallizations. To prepare from these crystals pure oxanilic acid, they are boiled with baryta-water; the oxanilate of baryta, which is formed after cooling, is washed with cold, and dissolved in boiling water, and decomposed with dilute sulphuric acid, an excess being carefully avoided; the filtrate, on being concentrated, deposits beautiful plates of oxanilic acid. This acid may be obtained also by dissolving crystals of oxanilate of aniline in ammonia, adding chloride of barium to the cold solution, and proceeding as just indicated; another method consists in decomposing the lime-salt (prepared by adding chloride of calcium to the ammonia-salt, boiling, and allowing it to crystallize), by means of a mixture of sulphuric acid and alcohol. —Crystallized oxanilic acid contains $C_{16} H_7 N O_6$ (= $C_{12} H_7 N$,

(1) Ann. Ch. Phys. [3] XXIV, 163; Ann. Ch. Pharm. LXVIII, 15; Compt. Rend. XXVII, 13, 165 (in abstr.); Instit. 1848, 221; J. Pharm. [3] XIV, 130.

(2) A. W. Hofmann has applied to the salts of aniline the method which has been used in preparing the *nitriles* (page 457). In treating oxanilide with anhydrous phosphoric acid, he obtained a small quantity of a compound, which he believes to be cyanogen with the adjunct $C_{12} H_4$. (Ann. Ch. Pharm. LXV, 56).

Oxalinic acid. $HO, C_2O_3 + HO, C_2O_3 - 2\,HO$ = binoxalate of aniline $- 2\,HO$); it is slightly soluble in cold, but dissolves easily in boiling water and in alcohol; the solution reddens litmus. Oxanilic acid is not decomposed by ebullition of the aqueous solution; concentrated aqueous potassa gradually decomposes it into aniline, which is separated, and oxalic acid (this effect is not produced by ammonia); when treated with hydrochloric, or dilute sulphuric acid, oxanilic acid yields an aniline-salt, oxalic acid being set free; when heated it disengages water, and a mixture of carbonic acid, and carbonic oxide, perfectly pure oxanilide remaining behind ($C_{16}H_7NO_6 = HO + CO + CO_2 + C_{14}H_6NO_2$).—The oxanilates are isomeric with the isatates; they are, however, colourless, but disengage aniline like the former, when heated with hydrate of potassa; a partial decomposition ensues, even on ebullition with aqueous potassa, or with concentrated acids.—*Oxanilate of ammonia*, $NH_4O, C_{16}H_6NO_5$, is easily obtained in beautiful plates, resembling oxanilic acid, which are but slightly soluble in cold water, or in alcohol, but dissolve easily on ebullition; treated with hydrochloric acid, and recrystallized, this salt yields tufts of *binoxanilate of ammonia*(1), which are slightly soluble in cold water. Both ammonia-salts are decomposed on heating (the former at 190°), with evolution first of ammonia, then of a mixture of carbonic acid and carbonic oxide, together with some aniline, a residue of oxanilide being left.—*Binoxanilate of aniline*, $C_{12}H_7N, 2\,HO, 2\,C_{16}H_6NO_5$, prepared by the above method, becomes colourless only after repeated crystallizations, when spiral, felted, lustreless needles are obtained, slightly soluble in cold water, but easily soluble in hot water, forming a very acid solution; on addition of hydrochloric acid to this solution, no oxanilic acid is precipitated, the same acid salt crystallizing invariably from the solution; when heated it is decomposed, yielding aniline, and the products of decomposition of oxanilic acid. —A solution of oxanilate of ammonia gives, with nitrate of protoxide of silver, *oxanilate of protoxide of silver*, as a white crystal-

(1) This paper affords to Gerhardt and Laurent an opportunity of repeating their opinion, previously enunciated, that in introducing the notion "Monobasic and bibasic acids," no definite characteristics of these acids had been indicated. In their opinion, monobasic acids are not capable of forming amidogen- and ether-acids; they cannot be converted into anhydrides (so-called anhydrous acids), and yield only neutral amides and ethers, 1 vol. of whose vapour contains the elements of 1 vol. of alcohol-vapour. Bibasic acids are those which, in addition with neutral ethers and amidogen-compounds, are likewise capable of forming amidogen- and ether-acids as well as anhydrides; 1 vol. of vapour of these ethers contains the elements of 2 vols. of alcohol-vapour.

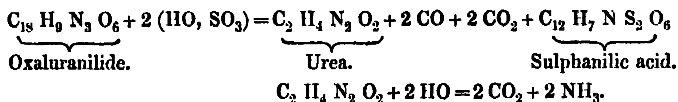
line precipitate, insoluble in cold, but soluble in boiling water; the solution deposits, on cooling, plates of an indistinct form. Concentrated solutions of oxanilate of ammonia, and chloride of calcium, give a precipitate of *oxanilate of lime*, which is soluble in boiling water, and crystallizes from this solution in tufts. *Oxanilate of baryta* is obtained in a similar manner by chloride of barium; a boiling solution deposits small brilliant plates, exhibiting rhombic forms under the microscope. The silver-, lime-, and baryta-salts (the lime-salt was very strongly dried) are represented by the formula, $MO, C_{16} H_6 NO_5$.

Oxaluranilide.

Oxaluranilide.—Laurent and Gerhardt are of opinion that oxaluric acid, obtained by Wöhler and Liebig, in their investigations of uric acid, has a constitution analogous to that of the amidogen-, or anilidogen-acids, inasmuch as it contains the elements of binoxalate of urea — 2 HO, and actually yields, on ebullition, oxalic acid and urea; urea, accordingly, would present a deportment similar to that of ammonia and aniline, and the term urides might be applied to the compounds analogous to the amides and anilides. Parabanic acid, in their opinion, is no acid, but stands to oxaluric acid (which is known to arise from parabanic acid by the assimilation of water) in the relation which exists between camphorimide, and camphoramic acid. They find this view confirmed by the rapid conversion of parabanic acid into *oxaluranilide*. Finely powdered parabanic acid, when slightly heated with dry aniline, directly yielded a crystalline mass, no water being evolved; the product was boiled with alcohol, to dissolve out aniline and parabanic acid, which might have escaped the action, when difficultly soluble oxaluranilide remained behind. When washed and dried, this substance is a white crystalline powder, which, under the microscope, is resolved into needles, exhibiting slightly the lustre of mother-of-pearl, and containing, $C_{18} H_9 N_3 O_6$ ($= C_{12} H_7 N + C_6 H_2 N_2 O_6$, aniline + parabanic acid). Oxaluranilide is formed also, by adding aniline to a boiling solution of parabanic acid, when, after a few seconds, it separates as crystalline flakes; it is inodorous and tasteless, insoluble in boiling water, and almost insoluble in boiling alcohol; when heated, it fuses, and is decomposed, at a still higher temperature, with evolution of pungent vapours, in which hydrocyanic acid may be recognized; when gently heated with hydrate of potassa, it disengages aniline and ammonia. Oxaluranilide dissolves easily in concentrated sulphuric acid; the solution evolves, on application of heat, carbonic oxide and carbonic acid, without blackening; the residuary mixture, when exposed to moist air, deposits, after

Succinanile, succinanilic acid and succinanilide.

some time, crystals of bisulphate of ammonia, whose mother-liquor, on dilution with water, and addition of chromic acid, exhibits the reddish-brown colouration, characteristic of sulphanilic acid.



$$\underbrace{C_{18}\,H_9\,N_3\,O_6}_{\text{Oxaluranilide.}} + 2\,(HO,\,SO_3) = \underbrace{C_2\,H_4\,N_2\,O_2}_{\text{Urea.}} + 2\,CO + 2\,CO_2 + \underbrace{C_{12}\,H_7\,N\,S_2\,O_6}_{\text{Sulphanilic acid.}}$$

$$C_2\,H_4\,N_2\,O_2 + 2\,HO = 2\,CO_2 + 2\,NH_3.$$

Succinanile, Succinanilic Acid, and Succinanilide.—A mixture of water, succinic acid, and aniline, yields easily succinate of aniline, crystallizing in beautiful, slightly rose-coloured needles (oblique rectangular prisms), which are readily soluble in water and alcohol. If powdered succinic acid be treated with dry aniline, the mixture fuses gradually, water and an excess of aniline being evolved; the mass, after having been in a state of fusion for eight or ten minutes, solidifies, after cooling, into an aggregate of spherically-grouped needles. This product is treated with a considerable quantity of boiling water, which dissolves the larger portion, and deposits, on cooling, colourless plates of *succinanile;* the residue remaining after treatment with water is *succinanilide.*—Succinanile, when crystallized from alcohol, presents itself in form of long felted needles; it contains $C_{20}\,H_9\,N\,O_4$ (= $C_{12}\,H_7\,N$, HO, $C_4\,H_2\,O_3$ + HO, $C_4\,H_2\,O_3$ — 4 HO, bisuccinate of aniline — 4 HO), and stands to aniline in the same relation as d'Arcet's *bisuccinamide* (succinimide) to ammonia; succinanile fuses at 155°, it is insoluble in cold water, easily soluble in alcohol and ether; an aqueous solution of potassa does not act upon it, with solid hydrate of potassa, however, it evolves at once aniline; it is readily soluble in nitric and hydrochloric acids; when heated it appears to sublime without decomposition. When boiled with an aqueous solution of ammonia, succinanile is converted into *succinanilic acid;* for this purpose it is dissolved in dilute boiling ammonia, to which some alcohol has been added. On boiling this solution, until the latter be expelled, and neutralizing with nitric acid, long plates of succinanilic acid are deposited on cooling, which may be purified by recrystallization from alcohol. The composition of succinanilic acid is $C_{20}\,H_{11}\,N\,O_6$ (succinanile + 2 HO); it dissolves but slightly in cold, more readily in boiling water (the solution reddening litmus), and easily in alcohol and ether; it fuses at 157°, and solidifies with crystalline texture; when exposed to a higher temperature it is decomposed into water and succinanile, which sublimes. Succinanilic acid is readily soluble in potassa, (when fused with potassa it disengages aniline) and in ammonia; succinanilate of ammonia crystallizes but very indistinctly; it is easily

soluble in water, yielding a solution, which is not precipitated by chloride of calcium, and scarcely troubled by chloride of barium. With a dilute solution no precipitate whatever takes place; succinanilate of baryta being easily soluble, especially in boiling water. Nitrate of protoxide of silver gives, with succinanilate of ammonia, a white precipitate of succinanilate of silver ($AgO, C_{20} H_{10} NO_5$), which is insoluble in water; with the sulphates of the protoxides of iron and copper, respectively, a whitish-yellow and a blue precipitate is produced. From the soluble succinanilates crystalline succinanilic acid is precipitated on addition of mineral acids. Succinanile, succinanilic acid and succinanilide.

Succinanilide.—*Succinanilide* (see p. 464) is easily soluble in boiling alcohol; the solution deposits small needles, which contain $C_{16} H_8 NO_2 = (C_{12} H_7 N, HO, C_4 H_2 O_3 — 2 HO$, succinate of aniline $— 2 HO)$; it fuses only at 220°, is insoluble in water, but dissolves readily in alcohol and ether; when fused with potassa it disengages aniline.

Suberanilide and Suberanilic Acid.—On heating a mixture of water, aniline and suberic acid, no action takes place; on fusing, however, a mixture of about equal volumes of dry aniline and fused suberic acid, water is disengaged, while the acid dissolves. On exposing the mixture for about ten minutes to a temperature closely approaching its boiling-point, and adding an equal volume of alcohol, a liquid is obtained, which readily solidifies to a crystalline mass. The whole is now dissolved in boiling alcohol, from which, on cooling, scales of *suberanilide* are separated, exhibiting the lustre of mother-of-pearl; the separation of this substance is promoted by the addition of water, the mother-liquor retains *suberanilic acid*. Suberanilide appears under the microscope in form of rectangular scales; it is insoluble in water, slightly soluble in cold alcohol, but readily in boiling alcohol and ether. Its composition is $C_{20} H_{12} N O_2 = (C_{12} H_7 N, HO, C_8 H_6 O_3 — 2 HO$, suberate of aniline $— 2 HO)$. It fuses at 183°; ammonia or boiling potassa-solution have no effect upon it; when fused with solid hydrate of potassa it disengages aniline; when distilled it yields an oil which solidifies on cooling, a slight residue of carbon remaining behind.—*Suberanilic acid* is obtained by evaporating the alcoholic solution, which was mentioned above, when after expulsion of the alcohol a brownish oil is separated, which solidifies on cooling. It is purified by dissolving in boiling aqueous ammonia; the suberanilate of ammonia, when decomposed with hydrochloric acid, yields the acid colourless; from the boiling solution it separates as a slightly coloured oil, which solidifies on

Suberanilide and suberanilic acid.

cooling. It presents itself in small plates, exhibiting no regular form, not even under the microscope, and has the composition $C_{28}H_{19}NO_6 = (C_{12}H_7N, 2HO, 2C_8H_6O_3 - 2HO$, bisuberate of aniline $- 2HO)$; it fuses at 128°, and solidifies with crystalline texture, it is insoluble in cold water, and dissolves but very little in boiling water, which assumes an acid reaction; it is readily soluble in ether. When fused with hydrate of potassa it disengages aniline, when distilled it yields a thick oily substance, which partly solidifies on cooling, a considerable residue of carbon remaining behind. (The distillate contains aniline; which may be removed by ether, when a white powder, probably *suberanile* is left, which dissolves in much boiling alcohol or ether, from which solutions it is deposited in crystals; it is insoluble in boiling potassa- or ammonia-solution, and is decomposed by fusion with hydrate of potassa, when aniline is evolved). Suberanilate of ammonia crystallizes in small grains, which are pretty soluble in water; the solution is not coloured by chloride of lime; it gives with nitrate of protoxide of silver a white precipitate of suberanilate of protoxide of silver $(AgO, C_{28}H_{18}NO_5)$, which is insoluble in water, and turns rapidly violet when exposed to the light; with chloride of calcium, chloride of barium and lead-salts, white precipitates are produced, with salts of protoxides of copper and iron, respectively a light-blue, and a whitish-yellow salt is formed.

Phtalanile and Phtalanilic Acid.—Dry aniline comports itself with phtalic acid, as does ammonia. On fusing a mixture of phtalic acid and aniline, a crystalline mass is obtained on cooling, which is powdered and purified by treatment with boiling alcohol, when *phtalanile* (corresponding to phtalimide) is left, as a crystalline powder; it is still farther purified by distilling, and dissolving the distillate in boiling alcohol, from which beautiful needles of phtalanile are deposited. It contains $C_{28}H_9NO_4 = (C_{12}H_7N, 2HO, C_{16}H_4O_6 - 4HO$, biphtalate of aniline $- 4HO)$, fuses at 203°, and sublimes, even before fusion, in splendid needles. It is insoluble in water; when fused with hydrate of potassa, it yields aniline. On boiling with aqueous ammonia, to which some alcohol has been added, the ebullition being continued for some time, even after solution has taken place, and neutralizing the liquid, while still hot, with nitric acid, phtalanilic acid is separated in thin plates; it contains $C_{28}H_{11}NO_6$ (phtalanile + 2HO), and is insoluble in cold, more soluble in boiling water, the solution assuming an acid reaction, and easily soluble in alcohol and ether. Phtalanilic acid fuses at 192°, but even at this temperature phtalanile is evolved. Phtala-

nilate of ammonia yields white precipitates with nitrate of protoxide of silver, and acetate of protoxide of lead; the solution is not changed by chloride of calcium, or nitrate of baryta; when fused with hydrate of potassa, phtalanilic acid disengages aniline.

Camphoranile and camphoranilic acid.

Camphoranile and Camphoranilic Acid.—Aniline, and so called anhydrous camphoric acid, do not combine in the cold; on heating, a product is obtained, which solidifies into a glacial mass, insoluble in alcohol; when treated with a boiling solution of ammonia *camphoranilic* acid is dissolved, *camphoranile* remaining behind.—The latter (corresponding to camphorimide) is deposited, from an ethereal solution, in needles, which appear to be volatile, without decomposition; they contain $C_{32} H_{19} N O_4 = (C_{12} H_7 N, 2 HO, 2 C_{10} H_7 O_3 - 4 HO$, bicamphorate of aniline $- 4 HO)$. It fuses at 116°, it is insoluble in cold, slightly soluble in boiling water, easily soluble in alcohol and ether. The solution in much water, to which some alcohol has been added, deposits brilliant needles, sometimes of an inch in length. The same solution, when neutralized with ammonia, yields, with nitrate of protoxide of silver, a crystalline precipitate, which is probably camphoranile-protoxide of silver. Camphoranile is not altered by potassa-solution; fusing hydrate of potassa disengages aniline. It is acted upon by concentrated ammonia, to which some alcohol has been added; the solution deposits needles of camphoranilate of ammonia.—The ammoniacal solution of camphoranilic acid, obtained as above-stated, deposits, on cooling, needle-shaped crystals, which do not crystallize well from water. The solution, when mixed with nitric acid, gave a flocculent precipitate of camphoranilic acid, which, on washing with boiling water, was converted into a soft resinous mass. This mass when dissolved in ammonia and alcohol, refused to crystallize; the solution, when evaporated, and mixed with water, deposited a portion of the acid. The resinous acid, when boiled with water, softens, fuses, and solidifies, with crystalline texture, after boiling for a considerable time; it is slightly soluble in boiling water, to which some alcohol has been added; on cooling, the acid is deposited in white needles, unless too much alcohol has been added, when it separates in the oily state. Camphoranilic acid thus presents itself in two states, the crystalline, and the amorphous; in both states it contains $C_{32} H_{21} N O_6$ (camphoranile $+ 2 HO$). When heated, it is decomposed into aniline, and so called anhydrous camphoric acid. On treatment with concentrated sulphuric acid, carbonic oxide is disengaged; on fusion with hydrate of potassa, it yields aniline. Camphoranilate of ammonia appears to exist, likewise,

Carbanilic or anthranilic acid.

in the crystalline and amorphous states; its solution gives, with nitrate of protoxide of silver, a white precipitate of camphoranilate of silver ($AgO, C_{32}H_{20}NO_5$), which is but slightly soluble in water. Chlorides of calcium and barium produce no precipitate.

Carbanilic or Anthranilic Acid.—The acids analogous to camphoranilic acid, contain the elements of aniline and of the so called anhydrous acid; camphoranilic acid is decomposed, accordingly, by heat. Fritzsche's anthranilic acid, when rapidly heated, splits into aniline and carbonic acid ($C_{14}H_7NO_4 = C_{12}H_7N + 2CO_2$), which induces Laurent and Gerhardt to consider it as an analogue of the acids in question, as *carbanilic acid.*

Sulphocarbanilide.—At a former period, A. W. Hofmann(1), and subsequently, Laurent(2), had prepared *sulphocarbanilide* ($C_{13}H_6NS$) by the direct action of bisulphide of carbon on aniline, when hydrosulphuric acid is evolved ($C_{12}H_7N + CS_2 = C_{13}H_6NS + HS$). The same compound, according to Hofmann, is formed also by the action of heat on hydrosulphocyanate of aniline. Laurent and Gerhardt find that it may be likewise prepared by distilling a mixture of aniline, sulphocyanide of potassium, and sulphuric acid, when sulphocarbanilide passes over, sulphate of ammonia being formed (the sulphuric acid liberates hydrosulphocyanic acid, $C_2NHS_2 + 2C_{12}H_7N = 2C_{13}H_6NS + NH_3$). The distillate is purified by recrystallization from alcohol.

On evaporating an aqueous solution of hydrosulphocyanic acid and aniline to syrupy consistency, and treating afterwards with boiling alcohol, small needles, insoluble in water, are obtained on its cooling; they are formed, however, in so small a quantity as to preclude the possibility of a more minute examination; when heated, they evolve ammonia and an oil, which solidifies (sulphocarbanilide), only a small amount of carbon being left behind.—A mixture of aniline and alcohol does not dissolve hydropersulphocyanic acid; with dry aniline, however, this acid fuses, on heating, into a mass, which solidifies with crystalline texture. The product is insoluble in water, but dissolves in boiling alcohol and ether; it is a mixture of sulphur and a peculiar substance, which is difficult to purify. It may be separated, though still contaminated with sulphur, by boiling with slightly alkaline water, filtering, and neutralizing with hydrochloric acid; this substance is soluble in boiling alcohol, from which it crystallizes on cooling; it is likewise soluble in ether. The nature of this compound is not sufficiently examined.

(1) Ann. Ch. Pharm. LVII, 265. (2) Loc. cit. p. 461.

Laurent and Gerhardt conclude this investigation with general remarks upon the formation and the properties of the anilidogen-compounds, whose composition they consider as a new confirmation of Gerhardt's(1) view respecting the capacity of saturation of the conjugated substances, and close with a synoptical table containing the corresponding amides, anilides, and ethers.

(1) The notion of "conjugated compounds" has been introduced into science by the observation, that, in the formation of compounds, the chemical properties of the constituents are not always balanced, but that, on the contrary, the chemical character of one of the constituents is frequently still perceptible in the compound. Laurent and Gerhardt believe that this notion is definite and unequivocal only, if conceived under their peculiar acceptation of the term. According to their definition, those compounds are conjugated which are formed by the direct union of two substances, with elimination of the elements of water, and which may be reconverted again into the original constituents, by fixing again the elements of water; such compounds are, f. i., the amides, the anilides, and the various ethers. This definition, however, far from embracing the notion in the conception of science, is nothing but a formula of the processes of production and decomposition of a great number of conjugated compounds. Laurent and Gerhardt endeavour to express the properties of the newly-formed compounds by a general formula. They represent the capacity of saturation or the basicity B of a compound, *i. e.*, the number of equivs. of base, which are neutralized by 1 eq of the compound, by the formula $B = b + b' - 1$, in which b and b′ denote the basicity of the two constituents before combination took place, 0 the basicity of a neutral body, and 1, 2, 3, that of a monobasic, bibasic and tribasic acid. This expression tells us that monobasic acids can give rise to neutral ethers, amides, and anilides only, while bibasic acids produce neutral ether- amidogen- or anilidogen-acids.—Strecker (Ann. Ch. Pharm. LXVIII, 47) endeavoured to prove that Laurent and Gerhardt's definition of conjugated acids does not even embrace all those compounds, which these chemists consider as conjugated, while, on the other hand, it includes also a variety of substances which, according to their professed opinions, do not belong to this class of compounds. He farther showed, that in the case of various conjugated compounds, which are formed by the union of several equivalents of the one constituent, with one of the other, the formula, when directly applied, leads to erroneous data, results agreeing with experience being obtained only by the assumption of a successive formation of the conjugated compounds, (namely, that 1 eq. of a substance combines with 1 eq of another, the compound thus produced with a second, &c.), and lastly, that in several cases, for which the assumption of such a successive formation is inadmissible (phtalanile, succinimide, &c.), the calculated basicity does not agree with the result of observation. He proposed, as expressing the basicity of a conjugated compound, the formula $B = b + b' \quad \frac{n}{2}$, in which n represents the number of hydrogen-equivalents eliminated. For the validity of this formula he has adduced a great variety of examples.—In reply, Gerhardt (in his and Laurent's Compt. Rend. des Trav. Chim. 1849, 76) has endeavoured to demonstrate that the inferences of his definition of the term "conjugated compounds" need not always or need only partially be confirmed by experience, that such substances (formobenzoic acid, f. i.) as do not agree with his formulation, should not be considered as conjugated compounds in his acceptation of the term; and lastly, that the results of Strecker's law of basicity altogether agree with those of his (Gerhardt's) own, when applied in the manner noticed by Strecker. Gerhardt passes in silence over those cases in which the inadmissibility of this application has been pointed out by the German chemist.

Cinnanilide.

Cinnanilide.—Aniline, when mixed with chloride of cinnamyl (see p. 411), evolves a great deal of heat; an easily fusible volatile substance being formed, which crystallizes from alcohol in needles. According to Cahours(1), this substance is *cinnanilide,* and contains $C_{30} H_{13} N O_2$. When distilled with hydrate of potassa, it yields aniline and cinnamic acid.

Cumanilide was prepared by Cahours in a similar manner, by acting with aniline upon chloride of cumyl (see p. 410); it forms long needles resembling benzoic acid, and which are very difficultly soluble in alcohol; they contain $C_{20} H_{17} N O_2$.

Anisanilide $C_{28} H_{13} N O_4$ was obtained by Cahours, in white brilliant subliming needles, by the action of aniline upon chloride of anisyl (see p. 413).

Naphthalidides.—The preceding researches have proved, that aniline, similarly to ammonia, is capable of giving rise to a series of compounds, which may be considered as originating by elimination of hydrogen and oxygen from aniline-salts. Delbos(2) has shown that naphthalidine also is capable of producing similar derivatives.

Carbamide of Naphthalidine.—Neutral oxalate of naphthalidine, when subjected to dry distillation fuses with loss of water of crystallization; on increasing the temperature decomposition ensues, the fused mass intumesces, water, carbonic oxide and carbonic acid being evolved, while a mixture of naphthalidine and a compound corresponding to carbanilide distils. The *carbamide of naphthalidine* is purified by boiling continuously with alcohol, when it remains undissolved. (A still better process consists in heating binoxalate of naphthalidine to complete fusion, and purifying the mass in the manner just indicated). Naphthalidine-carbamide is a light white body, rapidly assuming a red tint when exposed to light; at 300° it distils with partial decomposition and deposition of carbon; it is insoluble in water, and but slightly soluble in boiling alcohol, from which it is deposited on cooling in form of a white powder, consisting of microscopic needles. It contains $C_{21} H_8 N O$, whence its formation is represented by the equation $C_{20} H_9 N, HO, C_2 O_3 = C_{21} H_8 N O + 2 HO + CO$ (the evolution of carbonic acid is but a secondary phenomenon). It is soluble in an alcoholic solution of potassa, from which it is reprecipitated on addition of water; dilute solutions do not act upon it.

(1) Loc. cit. p. 276.
(2) Ann. Ch. Phys. [3] XXI, 68; Compt. Rend. XXIV, 1091; J. Pharm. [3] XII, 237; Ann. Ch. Pharm. LXIV, 370; J. Pr. Chem. XLII, 244.

Sulphocarbamide of Naphthalidine.—On adding bisulphide of carbon to a solution of naphtalidine in absolute alcohol, the sides of the vessel are coated after one or two days with dendritic aggregations of a white crystalline substance; after some time the mixture blackens, and the mother-liquor contains hydrosulphate of naphthalidine. On employing very dilute solutions of naphthalidine and bisulphide of carbon in absolute alcohol, the compound is deposited in colourless, brilliant needles, which are purified by washing with hot alcohol. Delbos assigns the formula $C_{21} H_8 N S$ to this compound, which he calls *naphthalidine-sulphocarbamide* (his analysis, however, does not agree very well with this formula). The equation $C_{20} H_9 N + CS_2 = C_{21} H_8 N S + HS$ would illustrate the formation of this substance; it is insoluble in water and alcohol, and decomposes on application of heat; dilute acids have no effect upon it, when boiled with an alcoholic solution of potassa it is converted into naphthalidine-carbamide. Organic bases.

Organic Bases. Nicotine.—Schloesing(1) considers the following method as best adapted for the preparation of nicotine. The aqueous decoction of tobacco is concentrated to syrupy consistence, and agitated, while still hot, with two volumes of alcohol. After some time a thin liquid layer separates on the top, which is separated by decantation from the lower one, chiefly consisting of malate of lime. The alcoholic liquid is subjected to distillation, and the syrupy residue treated again with alcohol. This extract contains the whole of the nicotine; it is separated from the spirit and agitated, while still hot, with potassa, and after cooling, with ether, which takes up the nicotine along with some yellow colouring substances; from the ethereal solution the nicotine is precipitated by powdered oxalic acid, as oxalate, in the form of a syrupy mass, which is repeatedly washed with ether, and then agitated, first with potassa, and subsequently with ether; lastly, the ether is distilled off in the water-bath, and the residue exposed for several days to a current of dry hydrogen at a temperature of 140°, which separates the last traces of ether, water, and ammonia; on now distilling at 180° the nicotine is obtained pure and colourless.

Schloesing has ascertained the amount of nicotine in various kinds of tobacco, both French and American. According to his experiments 100 parts of unribbed tobacco from :

(1) Ann. Ch. Phys. [3] XIX, 230.

Nicotine.

		Nicotine.			Nicotine.
Dep. Lot . . .	contain	7·96	Alsace . .	contain	3·21
„ Lot-et-Garonne .	„	7·34	Virginia . .	„	6·87
„ Nord . . .	„	6·58	Kentucky . .	„	6·09
„ Ile-et-Vilaine .	„	6·29	Maryland . .	„	2·29
„ Pas-de-Calais .	„	4·94	Havannal . .	less than	2·00

Dried snuff still contains 2 per cent of nicotine; in snuff not dried, 33 per cent of water as an average are present, depressing the percentage of nicotine to 1·36. The leaves of tobacco contain nicotine in the form of a salt, for the aqueous extract has an acid reaction, and yields but very little nicotine to ether. In snuff nicotine is partly free, partly in form of a neutral or basic salt, most probably as acetate; the ammonia therein is likewise present in form of a salt, it is to these two salts that snuff owes its pungent effect on the mucous membrane of the nose.—The method employed by Schloesing for determining the amount of nicotine in tobacco is very simple, and, as shown by his experiments, perfectly trustworthy.

10 grms. of tobacco-powder, the moisture of which has been determined, are exhausted with ammoniacal ether, in a displacement-apparatus similar to those described by Payen and Mohr(1), and having a tubulated balloon of the capacity of $\frac{1}{6}$ of a litre, the ethereal extract is boiled in order to separate the ammonia and the remaining ether subsequently evaporated in the air. The residue, from which a soft resinous substance separates, is carefully neutralized by sulphuric acid of known strength. The quantity of sulphuric acid (SO_3) used, being represented by A, the amount of nicotine ($C_{20}\,H_{14}\,N_2$) B is obtained by the proportion 40 : 162 = A : B.

Nicotine has been analysed both by Schloesing and Barral(2) with the same result as formerly by Melsens; their numbers establish the formula $C_{20}\,H_{14}\,N_2$.

	Melsens.	Schloesing.	Barral.	$C_{20}\,H_{14}\,N_2$
C	74·3	73·77 — 73·40	73·69	74·08
H	8·8	8·62 — 8·89	8·86	8·64
N	17·3	— —	17·04	17·28

By determining the amount of sulphuric acid requisite for the complete neutralization of nicotine, and by ascertaining the quantity

(1) Vide p. 90 of Practical Pharmacy, by Mohr and Redwood. Taylor, Walton, and Maberley, London, 1849.

(2) Ann. Ch. Phys. [3] XX, 345; Compt. Rend. XXIV, 818; J. Pr. Chem. XLI, 466.

of carbonates of lime and baryta precipitated by carbonic acid from a salt of these alkaline earths, to which nicotine had been added, Schloesing obtained numbers, which agree with the formula $C_{20} H_{14} N$; the analysis of the platinum-salt led to the formula $C_{10} H_7 N$. In order to decide this question, Barral has determined the spec. grav. of the nicotine-vapour, for which he found the numbers 5·607 and 5·630. The theoretical density of the formula $C_{10} H_7 N$, which corresponds to 2 vols. of vapour only, is 5·578. Barral is convinced that the equivalent of nicotine, corresponds, like ammonia and aniline, to 4 vols. of vapour, and hence that it is represented by the formula $C_{20} H_{14} N_2$. Nicotine.

Nicotine absorbs moisture with great avidity; when exposed to the moist atmosphere its weight increases according to Schloesing by $\frac{1}{10}$th in one day; in an experiment of Barral, nicotine absorbed in three weeks 177 per cent of water. The whole of this water is evolved again in a dry atmosphere.

The spec. grav. of nicotine Barral found to be 1·033 at 4°; 1·027 at 15°; 1·018 at 30°; 1·0006 at 50°; and 0·9424 at 101°·5. 100 of nicotine dissolve at 100° 10·58 of sulphur, the liquid assuming a dark-brown colour; phosphorus is insoluble in nicotine.—When acted upon by chlorine nicotine evolves hydrochloric acid, and is converted into a blood-red liquid, which becomes colourless when exposed to solar irradiation, and deposits needles at 8°; on addition of water a white body is separated.

Nicotine and Protochloride of Platinum.—On adding nicotine gradually to a gently warmed acid solution of protochloride of platinum, and agitating so as to avoid the disengagement of too much heat, Raewsky(1) obtained an orange-yellow, crystalline compound (*a*). The mother-liquor yielded on evaporation another combination (*b*) in right prisms of a red colour. The latter may be also produced by dissolving the orange-yellow crystals in the mother-liquor, and evaporating *in vacuo*.—*a*) *Orange-yellow salt* $PtCl, C_{10} H_7 N, 2 HCl$; it is insoluble in cold, but dissolves in boiling water, in hydrochloric and nitric acid, and crystallizes from these solutions without change in composition; the solution in hydrochloric acid deposits splendid orange-yellow rhombic prisms, that in nitric acid yields small yellow crystals. When treated with boiling water an amorphous residue is left, which according to Raewsky's analysis has the same composition. The salt is perfectly soluble in nicotine;

(1) Ann. Ch. Phys. [3] XXV, 332; J. Pr. Chem. XLVI, 470; Compt. Rend. XXVII, 609, (in abstr.).

Nicotine and protochloride of platinum. on evaporation the solution forms a deliquescent gelatinous msss, miscible with water, alcohol, ether, and acids, but not crystallizable; on addition of concentrated sulphuric acid the platinum-salt turns white.—(*b*) *Red salt* PtCl, C_{10} H_7 N, HCl. It is but slightly soluble in cold, but dissolves in boiling water; the solution deposits pale yellow scales, which have the same composition as the red modification. It is insoluble in alcohol and ether; it dissolves in hydrochloric and nitric acids, and is decomposed by the latter on heating. On addition of concentrated sulphuric acid it turns brown.

Quinine.—According to Laurent(1) quinine has the formula C_{38} H_{22} N_2 O_4, which requires 73·4 of carbon, and 7·1 of hydrogen. He found 73·27—73·57 of carbon, and 7·14—7·07 of hydrogen. The platinum-salt C_{38} H_{22} N_2 O_4, 2 HO, 2 HCl + 2 $PtCl_2$ requires 26·5 per cent of platinum (Laurent found 26·4; Liebig 26·4—26.5—26·6; Gerhardt 26·3), and 29·6 per cent of chlorine, (Gerhardt found 29·5).

Hyposulphite of Quinine.—Winckler(2) showed, that hydrochlorate of quinine yields with hyposulphite of soda a flocculent precipitate, which is insoluble in cold water, and crystallizes from an alcoholic solution in needles; at 100^0 these crystals lose water of crystallization, and fall to a strongly electrical powder. C. M. Wetherill(3) has analysed this salt; he arrived at the formula C_{38} H_{24} N_2 O_4, S_2 O_2, HO, according to which, quinine would contain 2 equivs. of hydrogen more than Laurent assumes. Wetherill found 6·65—6·79 per cent of hydrogen; the above formula requires 6·77 per cent; the theoretical percentage of C_{38} H_{22} N_2 O_4, S_2 O_2, HO is 6·27; hence Wetherill's analysis would rather support the latter formula, inasmuch as the hydrogen-determinations exhibit usually an excess.

Phosphate of Quinine.—By dissolving quinine in gently warmed phosphoric acid Anderson(4) obtained soft satiny needles, neutral to vegetal colours, which contained 61·85 per cent of carbon, and 6·81 of hydrogen. He believes it to contain (at 100^0) 3 C_{20} H_{12} N O_2, 3 HO, PO_5. At 121^0 the salt of one preparation lost 7·88 per cent, that of another 15·3 per cent of water, which would indicate the existence of two salts.—Anderson has not determined the phosphoric acid, whence it remains doubtful, whether the salt

(1) Ann. Ch. Phys. [3] XIX, 363; Ann. Ch. Pharm. LXII, 95; Compt. Rend. XXIV, 219; J. Pr. Chem. XL, 400.

(2) Jahrb. Pr. Chem. XV, 281.

(3) Ann. Ch. Pharm. LXVI, 150.

(4) Ibid. 55, (comp. "Strychnine").

actually contains 3 equivs. of quinine; his analysis, if Laurent's formula be adopted, agrees best with 3 $C_{19}H_{11}NO_2$, PO_5; which requires 61·8 per cent of carbon, and 6·2 of hydrogen. Phosphate of quinine.

Hydrosulphocyanate of Quinine.—According to Dollfus(1) two salts exist, a white one and a yellow one which is resin-like, and agglutinates; they invariably crystallize together.

Hydroferro- and Hydroferricyanate of Quinine.—On mixing alcoholic solutions of hydroferrocyanic acid and of quinine, an orange-yellow crystalline precipitate is produced which, according to Dollfus(2), contains 52·9 per cent of carbon, 6·0 of hydrogen, and 9·1 of iron; these numbers lead to the formula $C_{20}H_{12}NO_2$, H_2 Cfy + 3 HO, which requires 52·5 of carbon, 5·7 of hydrogen, and 9·4 of iron. This compound, however, is very easily decomposed, and cannot be adduced in favour of one or the other of the quinine-formula; if we adopt Laurent's formula, the above numbers would be best represented by the formula $C_{38}H_{22}N_2O_4$, 2 H_2 Cfy + HO, which requires 53·2 of carbon, 5·3 of hydrogen, and 9·9 of iron. Hydrochlorate of quinine produces with ferricyanide of potassium a crystalline precipitate resembling *aurum musivum*, and containing, according to Dollfus, 54·6 of carbon, 5·4 of hydrogen, and 9·8 of iron.

Adulteration of Quinine.—Stresemann(3) has observed adulterations of quinine with 30—40 per cent of salicine, Sckeyde(4) with 10—18 per cent of milk-sugar, Winckler(5) with 40 per cent of carbonate of lime.

Substitute for Quinine.—Spatzier(6) has lately recommended for this purpose *Variolaria amara* Ach. (*Persutaria communis DC.*), which in 1832 had been proposed by Alms as a remedy in intermittent fever. Knop(7) observes, on this occasion, that possibly similar medicinal properties may be possessed by the very bitter salts of cetraric and stictic acids, which are probably closely allied to picrolichenin, extracted by Alms from *V. amara.*—Winckler(8) repeatedly recalls attention to purified quinoidine, and also to quinidine and cinchonine; the latter especially, is stated on the authority of distinguished physicians, to possess in the form of salts,

(1) Ann. Ch. Pharm. LXV, 215.
(2) Ibid. 224.
(3) Arch. Pharm. [2] LII, 151.
(4) Ibid. [2] LVI, 171.
(5) Repert. Pharm. [2] XLVII, 403; Jahrb. Pr. Pharm. XV, 165.
(6) Arch. Pharm. [2] LVI, 166.
(7) Pharm. Centr. 1848, 943.
(8) Jahrb. Pr. Pharm. XVII, 83.

Cinchonine. never failing febrifuge properties.—Bebeerine likewise deserves attention as a substitute for quinine.

Cinchonine.—Laurent(1) has altered also the formula of cinchonine, by which its relation to quinine is re-established. He proposes $C_{38} H_{22} N_2 O_2$ (theory 77·55 of carbon, 7·48 of hydrogen; experiment 77·22—77·36 of carbon, and 7·47—7·51 of hydrogen). This formula is supported by the numbers obtained by Regnault in analysing the sulphate, iodate and nitrate of cinchonine, and by the investigation of the subsequent cinchonine-compounds. The platinum-salt is $C_{38} H_{22} N_2 O_2$, 2 HCl, 2 Pt Cl_2 + 2 HO (theory 27·26, experiment 27·2—27·3 of platinum). The 2 equivs. of water are evolved at 140°.

Hydrochlorate of Cinchonine crystallizes from aqueous alcohol containing a slight excess of acid, on slow evaporation, in tables with a rhombic base, whose acute angles are truncated. Laurent's(2) analysis led to the formula $C_{38} H_{22} N_2 O_2$, 2 HCl. It is readily soluble in water, less so in alcohol; the solution reddens litmus.

Hydrosulphocyanate of Cinchonine.—By the analysis of this salt, which crystallizes in brilliant needles, Dollfus(3) has confirmed Laurent's cinchonine-formula. He found in 100 parts 67·86 of carbon, and 6·63 of hydrogen. The formula $C_{38} H_{22} N_2 O_2$, H C_2 N S_2 requires 67·9 of carbon, and 6·63 of hydrogen. Hence the equivalent of cinchonine is 294. Dollfus found 289.

Hydroferro- and Hydroferricyanate of Cinchonine.—These salts have been likewise analysed by Dollfus(4). His results add a new confirmation to Laurent's formula of the base. Hydroferrocyanate of cinchonine contains $C_{38} H_{22} N_2 O_2$, 2 H_2 Cfy + 4 HO, the hydroferricyanate has the formula $C_{38} H_{22} N_2 O_2$, H_3 Cfy_2 + 4 HO.—Both salts are crystalline precipitates, which, when heated, either alone, or in aqueous solutions, are decomposed into hydrocyanic acid, and a bluish residue; with solutions of protoxide and sesquioxide of iron, they exhibit the same deportment as the corresponding potassium-compounds.

Chlorocinchonine and Bromocinchonine.—On passing a current of chlorine into a warm concentrated solution of hydrochlorate of cinchonine, Laurent(5) obtained a heavy crystalline powder, which

(1) Ann. Ch. Phys. [3] XIX, 365, (for the other quotations, *see* p. 474).
(2) Ibid. [3] XXIV, 302; Ann. Ch. Pharm. LXIX, 9.
(3) Ann. Ch. Pharm. LXV, 222.
(4) Ibid. 225.
(5) Ann. Ch. Phys. [3] XXIV, 302; Ann. Ch. Pharm. LXIX, 9; J. Pharm. [3] XIV, 456.

Chlorocinchonine and bromocinchonine.

after recrystallization from boiling water, was found to be pure hydrochlorate of chlorocinchonine, $C_{38} H_{20} Cl_2 N_2 O_2, 2 HCl$. It is, like the subsequent compounds, isomorphous with hydrochlorate of cinchonine, slightly soluble in water and soluble in 50 parts of alcohol. Chlorocinchonine, precipitated from this salt by means of ammonia, contains $C_{38} H_{20} Cl_2 N_2 O_2$ (theory 19·5 per cent of chlorine; experiment 18·9); it is crystallizable, and yields, when distilled with potassa, chinoline free from chlorine. The platinum-salt $C_{38} H_{20} Cl_2 N_2 O_2, 2 HCl, 2 Pt Cl_2 + 2 HO$, is a pale-yellow powder. Hydrobromate of chlorocinchonine $C_{38} H_{20} Cl_2 N_2 O_2, 2 H Br$, is difficultly soluble. By treating hydrochlorate of cinchonine with bromine, Laurent obtained a mixture of two compounds, containing different quantities of bromine. One of these compounds forms a hydrochlorate, soluble in alcohol, and contains $C_{38} H_{21} Br N_2 O_2$; the other, which Laurent designates as sesquibromocinchonine, is probably a mixture of the former with dibromocinchonine, $C_{38} H_{20} Br_2 N_2 O_2$, both compounds, in consequence of their isomorphism, crystallizing together. On analysis, the formula $C_{38} H_{\frac{41}{2}} Br_{\frac{3}{2}} N_2 O_2$ was obtained, which was confirmed by the study of the hydrochlorate and of the platinum-salt. Laurent farther mentions a hydrobromochlorate of bromocinchonine, $C_{76} H_{41} Br_3 N_4 O_4, 2 HCl, 2 H Br$, which is produced by the action of bromine upon hydrochlorate of cinchonine. The crystalline form of the isomorphous compounds above enumerated, is a right, rhombic prism ∞P, which is shortened to a table by the predomination of the terminal plane $0 P$; the more acute edges of the prism are replaced by two planes $\breve{P} \infty$, tangent in points. In measuring the angles, Laurent found for:

	$\infty P : \infty P$	$\breve{P} \infty : 0 P$
$C_{38} H_{22} N_2 O_2, 2 HCl$	101°	137 —138°
$C_{38} H_{20} Cl_2 N_2 O_2, 2 HCl$	106	136½—137½
$C_{38} H_{20} Cl_2 N_2 O_2, 2 HBr$	104	137
$C_{38} H_{\frac{41}{2}} Br_{\frac{3}{2}} N_2 O_2, 2 HCl$	107—108	

Winckler(1) has shown, that cinchonine, when heated with an excess of concentrated sulphuric acid, loses its faculty of crystallizing, assuming the properties of amorphous cinchonine, which he had previously prepared from commercial quinoidine. The hydrochloric solution of amorphous quinine and cinchonine, is not affected by hyposulphite of soda, while the hydrochlorates of the crystalline bases yield directly crystalline precipitates.

(1) Jahrb. Pr. Pharm. XV, 281; Repert. Pharm. [2] XLVIII, 39[illegible].

Quinidine. According to Roder's(1) statement, quinoidine would be a compound of crystalline quinine and cinchonine with a resin, which could be separated by treating the alcoholic solution with protochloride of tin. It was proved, however, by Winckler(2) that pure amorphous quinine remains amorphous even after treatment with protochloride of tin, and that the crystalline bases, observed by Roder, must have been present in the specimens of quinoidine employed, which is invariably the case in the commercial article.

Quinidine.—In a Quina-bark, occurring in commerce, in the same packages as *Quina regia,* but having in its exterior the greatest resemblance to *Quina Huamalies,* Winckler(3) has observed a new organic base, which he calls *quinidine,* and which, according to his observations, is frequently present in commercial sulphate of quinine. From a large quantity of crude quinidine, obtained by Zimmer in manufacturing quinine, and consisting chiefly of quinine and the new alkaloid, Winckler separated quinine and a yellow resinous substance; the insoluble residue, when dissolved in alcohol of 80 per cent, treated with animal charcoal and slowly evaporated, yielded coloured crystals of quinidine, which were purified by conversion into sulphate, precipitation with carbonate of soda, edulcoration, and recrystallization from alcohol.

Quinidine is thus obtained in large crystals, possessing the lustre of glass; their form is a right four-sided prism, which is either rightly truncated or pointed by one or two planes. When rapidly deposited, it separates as a crystalline powder, which, under the microscope, appears as an aggregate of rhombic tables. When heated, it fuses; at a higher temperature a small portion sublimes, while the larger is decomposed, with evolution of a vapour, possessing the odour of kinone. The powder is scarcely electric. Quinidine is but slightly soluble in water, but dissolves readily in alcohol; 100 parts of ether dissolve only 0·69 of the base. It neutralizes the acids perfectly; an excess of acid gives rise to an opalescence of the solution, just as with quinine. The solutions have the same bitter taste as quinine. Quinidine does not lose in weight when exposed to 100°. Both the basic sulphate and the platinum-salts have, according to Winckler, the same composition as the corresponding compounds of quinine; the neutral sulphate, dried in the air, loses,

(1) Mittheilungen des Schweizer Apotheker-Vereins, I, 31; Repert. Pharm. [3] I, 100.

(2) Jahrb. Pr. Pharm. XVII, 32.

(3) Repert. Pharm. [2] XLVIII, 384; XLIX, 1.

Pseudo-quinine.

when fused, 19 per cent of water; it contains 16·55 per cent of sulphuric acid. Winckler supposes that quinidine has the same composition as quinine; this question has to be decided by more accurate analytical experiments.

Pseudoquinine.—In an extract of Quina, of unknown origin, Mengarduque(1) has found an organic base, which both in deportment and composition, essentially differs from quinine, cinchonine, or cinchovatine; none of the three latter substances were present. This substance neutralizes the acids perfectly, and decomposes ammonia-salts; it is insoluble in ether and water, but dissolves in alcohol, from which it crystallizes in irregular prisms. Its solution in chlorine-water assumes, on addition of ammonia, a reddish-yellow colour, while quinine becomes green. It is tasteless; the sulphate, likewise, which crystallizes in flat prisms, has scarcely a bitter taste. On analysing the base, 76·5—76·7 per cent of carbon, 8·1—8·2 of hydrogen, 10·2—10·4 of nitrogen, and 5·2—4·7 of oxygen were obtained.

Morphine.—Laurent(2) has again analysed this base. He proposes the formula $C_{34}\ H_{19}\ N\ O_6$, which contains 1 equivalent of hydrogen more than Liebig's formula. (Theory, 71·58 of carbon and 6·66 of hydrogen; experiment, 71·63—71·59 of carbon and 6·58—6·66 of hydrogen). Hence it would differ from codeïne by 1 eq. of oxygen only, which the latter contains less.

Hydrosulphocyanate of Morphine has been analysed by Dollfus(3), who found the formula $C_{34}\ H_{18}\ N\ O_6,\ H\ C_2\ N\ S_2,\ HO$; according to his experiment, morphine contains even one of hydrogen less than Laurent's formula admits.

Amount of Morphine present in Opium.—Aubergier(4) has performed a series of experiments with varieties of poppy (*Papaver somniferum*), cultivated in 1844 and 1845, in Algeria. He proves that the quality of the opium prepared therefrom, *i. e.*, its amount of morphine, depends partly on the variety of the plant and partly on the maturity, more or less advanced, of the capsule at the time of collection. The milky juice is richest in morphine when the capsules are not completely ripe, and present still a green colour; as soon as they become yellowish-brown, the time for the opium-crop has passed. If care be taken in making the incisions into the poppy-

(1) Compt. Rend. XXVII, 221; J. Pr. Chem. XLV, 356; J. Pharm. [3] XIV, 343; J. Chim. Méd. [3] V, 17.
(2) Ann. Ch. Phys. [3] XIX, 361 (comp. p. 474).
(3) Ann. Ch. Pharm. LXV, 216.
(4) Ann. Ch. Phys. [3] XX, 303.

Amount of morphine present in opium.

heads, so as not to injure the pericarp, through which air might penetrate into the interior, the seeds still ripen, quite independent of the opium-crop. Aubergier effects this by means of an instrument containing four blades, which are so adjusted as to produce incisions of 1—2^{mm} only. The exuding milky juice is collected before it dries upon the capsule, by which the loss occasioned by rain is altogether prevented. The determination of morphine was effected according to Payen's method. Aubergier decolourized, however, his solution of morphine by animal charcoal, whereby his numbers became uncertain, inasmuch as organic bases are well known to be carried down by animal charcoal. He obtained the following results:

Variety of poppy.		Time of collection.		Morphine in 100 parts of opium containing 7·6 per cent of water.
White poppy . . .	1844.	1. collection	5.—11. July	8·570
ditto . . .	„	2. „	17.—20. July	1·520
Red poppy . . .	„		11.—13. July	10·690
White poppy . . .	„	1. „	9. July	6·630
ditto . . .	„	2. „	28. July	5·530
ditto . . .	„	3. „	13. August	3·270
Red poppy . . .	„	1. „	21. July	10 370
ditto . . .	1845.	2. „	26. July	10·649
ditto . . .	„	3. „	16. August	11·230
Oeillette	„	1. „	29.—30. July	17·833
ditto . . .	„	2. „	21. August	14·780

Sulphomorphide and Sulphonarcotide.—Arppe(1) described, in 1845, a white substance, becoming green when exposed to the atmosphere, which he had obtained by the action of an excess of sulphuric acid upon morphine. His analysis had led to the formula $4\,C_{35}\,H_{20}\,N\,O_6 + 5\,SO_3$. On the assumption of morphine being a conjugated ammonia-compound, Arppe conjectured that this substance contained anhydrous sulphate of ammonia, whence he proposed the following rational formula: $C_{35}\,H_{17}\,O_6,\ NH_3,\ SO_3 + 3\,(C_{35}\,H_{17}\,O_6,\ NH_3) + 4\,SO_3$.

Laurent and Gerhardt(2) have likewise analysed this compound; they consider it as neutral sulphate of morphine, *minus* 2 eq. of water, when the compound would belong to the class of amides and anilides. Their analysis yielded 63·0 per cent of carbon, 5·8 of hydrogen, and 5·4 of sulphur; the formula $C_{34}\,H_{18}\,N\,O_8\,S = C_{34}\,H_{18}\,NO_5,\ SO_3$ requires 64·5 of carbon, 5·7 of hydrogen, and 5·1 of sulphur. Lau-

(1) Ann. Ch. Pharm. LV, 96.

(2) Ann. Ch. Phys. [3] XXIV, 112; Compt. Rend. XXVII, 80; J. Pharm. [3] XIV, 302; Ann. Ch. Pharm. LXVIII, 358; J. Pr. Chem. XLV, 369.

Sulphomorphide and sulphonarcotide

rent and Gerhardt consider a loss of 1·5 per cent of carbon unavoidable in the analyses of uncrystallizable and difficultly combustible substances. They propose the designation *sulphomorphide* for this substance.—On treating narcotine with dilute sulphuric acid, Laurent and Gerhardt obtained a dark-green body, insoluble in water, but dissolving in alcohol, and exhibiting the same deportment as sulphomorphide, whence the name *sulphonarcotide*. Analysis yielded 59·1 per cent of carbon, 5·3 of hydrogen, and 3·6 of sulphur; the formula of neutral sulphate of narcotine, *minus* 2 equivs. of water, $C_{46} H_{25} N O_{14}, HO, SO_3, - 2 HO = C_{46} H_{24} N O_{13}, SO_3$, requires 60·2 of carbon, 5·2 of hydrogen, and 3·5 of sulphur. Morphine and narcotine cannot be reproduced from these compounds.

Cotarnine.—Laurent(1) proposes the formula $C_{26} H_{13} N O_6$ for this compound, which had been obtained from narcotine by Wöhler on treating it with sulphuric acid and binoxide of manganese, by Blyth on acting upon it with bichloride of platinum. He farther repeated the analysis of opianic acid, which together with hemipinic acid, is produced in the same process of oxidation; his analysis led him to the formula $C_{20} H_{10} O_{10}$, (theory, 57·15 per cent. of carbon and 4·77 of hydrogen; experiment, 57·10 of carbon and 4·88 of hydrogen), which contains 1 eq. of hydrogen less than Wöhler's formula. The formation of these substances from narcotine would then be represented by the following equation:



$$C_{46} H_{25} N O_{14} + O_4 = C_{26} H_{13} N O_6 + C_{20} H_{10} O_{10} + 2 HO.$$

Narcotine. Cotarnine. Opianic acid.

Opianic acid, by the absorption of 2 more equivs. of oxygen, is converted into hemipinic acid, $C_{20} H_{10} O_{12}$.—On adding together the formulæ of narcotine and cotarnine, 2 equivs. of narcogenine, $2 C_{36} H_{19} N O_{10}$ are obtained; or 2 equivs. of narcotine, by absorbing 4 equivs. of oxygen are converted into 2 equivs. narcogenine, 1 equiv. of opianic acid, and 2 equivs. of water.

Codeine.—The hydrosulphocyanate of codeine is obtained on adding hydrosulphocyanic acid to an alcoholic solution of this base. It forms needles, fusing at 100°, and containing, according to Dollfus'(2) analysis $C_{34} H_{19} NO_5, H C_2 NS_2 + HO$; (theory, 62·60 of carbon and 6·08 of hydrogen; experiment, 62·30 of carbon and 6·12 of hydrogen).

(1) Ann. Ch. Phys. [3] XIX, 370, (for the other quotations, *see* p. 474).
(2) Ann. Ch. Pharm. LXV, 217.

Papaverine.

Papaverine.—The residues of the preparation of morphine contain a new opium-base, which has been discovered by G. Merck(1), who proposes for it the name *papaverine*. This base contains $C_{40} H_{21} N O_8$; it is but slightly soluble in cold, more readily in hot spirits of wine and ether, and is deposited from these solutions in white, spear-like crystals, which act but slightly on reddened litmus. When in contact with concentrated sulphuric acid, they assume a blue colour.—The greater part of the salts are difficultly soluble in water; hydrochlorate of papaverine, $C_{40} H_{21} N O_8$, H Cl, crystallizes, according to H. Kopp's determination, in right rhombic prisms, with edges of 80° and 100°. From its aqueous solution, this salt is precipitated by hydrochloric acid in oily drops, which when left at a gentle temperature, are gradually converted into an aggregate of crystals. Sulphuric and nitric acids produce a similar deportment. The platinum-salt, $C_{40} H_{21} N O_8$, HCl, $PtCl_2$, is a yellow precipitate, insoluble in water and spirits of wine. Details respecting the preparation of the base, its chemical deportment and analysis, have not yet been communicated by G. Merck.

Piperine is isomorphous with morphine, according to a repeated analysis by Laurent(2), which confirms Regnault's formula $C_{34} H_{19} NO_6$.

Phosphate of Strychnine.—Th. Anderson(3) has described two compounds of phosphoric acid with strychnine.

On digesting strychnine, at a gentle heat, with moderately dilute phosphoric acid, as long as it is readily dissolved, radiated groups of long needles are deposited on cooling, which (at 127°) contain, $C_{44} H_{24} N_2 O_4$, HO, $PO_5 + 2$ HO, (theory, 59·14 of carbon and 6·04 of hydrogen; experiment, 59·05—58·72 of carbon and 5·97—5·96 of hydrogen). The crystallized salt loses, at 127°, 4 equivs (7·42 per cent) of water, (experiment, 7·95). It dissolves in 5—6 parts of water, and has an acid reaction.

If the solution of the acid salt be digested for some time with an excess of strychnine, and the product be recrystallized several times, large rectangular tables are obtained, which have no longer an acid they are $2 (C_{44} H_{24} N_2 O_4$, HO), HO, $PO_5 + 18$ HO. At

(1) Ann. Ch. Pharm. LXVI, 125; Arch. Pharm. [2] LVI, 312; Repert. Pharm. [3] I, 96; J. Pharm. [3] XV, 167.

(2) Ann. Ch. Phys. [3] XIX, 363; Ann. Ch. Pharm. LXII, 98.

(3) Chem. Soc. Qu. J. I. 55; Phil. Mag. [3] XXXIII, 163; Ann. Ch. Pharm. LXVI, 55; J. Pharm. [3] XIV, 49.

100° this compound loses 18 equivs. (17·6 per cent) of water of crystallization. Hydrosulphocyanate of strychnine.

Hydrosulphocyanate of Strychnine has been analysed by Dollfus(1), who confirms the formula of strychnine proposed by Gerhardt. The salt is obtained in the form of transparent difficultly soluble needles, on adding hydrosulphocyanic acid to an alcoholic solution of strychnine, or by decomposing a strychnine-salt by means of sulphocyanide of potassium. In this, as well as in all the other analyses, Dollfus availed himself of the insolubility of sulphocyanide of silver for determining the equivalents of the bases which he examined. He arrived exactly at the formula $C_{44} H_{24} N_2 O_4, H C_2 N S_2$, (theory, 67·81 of carbon and 6·14 of hydrogen; experiment, 67·70 of carbon and 6·39 of water).

Hydrochlorate of Strychnine and Cyanide of Mercury combine, according to Brandis(2), forming a crystalline precipitate, when both constituents are mixed. From hot solutions, the double compound is deposited in rectangular, four-sided tables, possessing the lustre of mother-of-pearl, and containing $C_{44} H_{42} N_2 O_4$, HCl + 4 Hg Cy.

Hydroferrocyanate of Strychnine was obtained by Brandis(3) on mixing neutral strychnine-salts with ferrocyanide of potassium, when a copious precipitate is formed, which consists of colourless crystals. From dilute solutions, light-yellow crystals, of from ½ to 1 inch in length, are deposited; their form is a rectangular, four-sided prism, with ends pointed by two planes in the direction of the edges. They contain, according to Brandis, $2 C_{44} H_{24} N_2 O_4, H_2 Cfy + 8 HO$. At 100° the compound loses 6 eqs. = 6·12 per cent of water.—With salts of iron, lead, and copper, it exhibits the same deportment as ferrocyanide of potassium.—On dissolving this salt in boiling water, or on heating the saturated aqueous solution to ebullition, strychnine crystallizes first, and subsequently

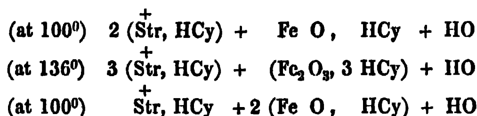
Hydroferricyanate of Strychnine is deposited. This compound is obtained likewise, by mixing a saturated solution of a strychnine-salt with ferricyanide of potassium, when beautiful, golden-yellow, brilliant crystals are separated, which resemble the preceding compound. They contain $3 C_{44} H_{24} N_2 O_4, H_3 Cfy_2 + 12 HO$. Of these 12 equivs. of water, 3 equivs. are lost *in vacuo*, 6 equivs. at 100°, and 8 equivs. at 136°. When heated more strongly, the compound is decomposed, with evolution of hydrocyanic acid. On boiling Prussian blue with strychnine, the hydroferricyanate is

(1) Ann. Ch. Pharm. LXV, 221. (2) Ibid. LXVI, 269.
(3) Ibid. LXVI, 257; Instit. 1848, 194.

Hydroferricyanate of strychnine.

likewise formed; a reaction which is intelligible by the deportment of the preceding compound on ebullition with water.

On adding hydroferricyanic acid to an alcoholic solution of strychnine, or of hydroferricyanate of strychnine, until the liquid assumes a slightly acid reaction, a white powder is precipitated, almost insoluble in water and alcohol, which differs both in its properties and constitution from the above compound. This substance has an acid reaction; on treatment with potassa it is converted into an amorphous, white mass, turning blue when exposed to the air, and on treatment with alcohol, decomposed into an amorphous, blue compound, hydroferrocyanate of strychnine and ferrocyanide of potassium. With boiling water, it yields a blue precipitate and hydroferricyanate of strychnine. Brandis proposes for this compound the formula $C_{44}\,H_{24}\,N_2\,O_4,\ Fe_2\,Cy_2,\ H_2\,Cy_2+5\,HO$, the only one agreeing with the results of his analysis. When considered as hydrocyanates, the compounds investigated by Brandis are represented by the following formulæ:



(at 100°) $2\,(\overset{+}{Str}, HCy) + Fe\,O,\ HCy + HO$

(at 136°) $3\,(\overset{+}{Str}, HCy) + (Fe_2\,O_3,\ 3\,HCy) + HO$

(at 100°) $\overset{+}{Str}, HCy + 2\,(Fe\,O,\ HCy) + HO$

When dried as far as possible without decomposition, these salts still contain 1 eq. of water.

Chlorostrychnine and Bromostrychnine.—On passing, according to Laurent(1), a current of chlorine into a gently-warmed solution of hydrochlorate of strychnine, it assumes a rose-red colour, while a resin-like substance separates. The solution, when carefully subjected to a fractional precipitation, by means of ammonia, yields a white precipitate, which gives with sulphuric acid a crystalline salt, of the formula, $C_{44}\,H_{23}\,Cl\,N_2\,O_4,\ HO,\ SO_3+7\,HO$, having a composition analogous to sulphate of strychnine.—By similarly acting with bromine upon hydrochlorate of strychnine, a bromostrychnine was obtained, in which less than 1 eq. of hydrogen ($\frac{8}{10}$) was replaced by bromine.

Phosphate of Brucine has been prepared by Anderson(2). It forms short, thin prisms, which are readily soluble in water, without action on vegetal colours, and fuse at 100°. When dried at 100°,

(1) Ann. Ch. Phys. [3] XXIV, 312; Ann. Ch. Pharm. LXIX, 14; J. Pr. Chem. XLVI, 52.

(2) Ann. Ch. Pharm. LXVI, 55, (comp. p. 482).

they contain $2\,C_{46}\,H_{26}\,N_2\,O_8$, HO, $PO_5 + 2$ HO. The water of crystallization was not determined.—On digesting acid phosphate of soda with brucine, a double salt is obtained, which, according to an analysis (the details of which have not been communicated), is approximately represented by, $\overset{+}{Br}$, HO, NaO, HO, PO_5.

Phosphate of brucine.

Hydrosulphocyanate of Brucine crystallizes in anhydrous plates upon addition of hydrosulphocyanic acid to a solution of brucine. The salt is readily soluble in water. According to Dollfus'(1) analysis, it contains $C_{46}\,H_{26}\,N_2\,O_8$, H C_2 N S_2, (theory, 63·57 per cent of carbon and 5·96 of hydrogen; experiment, 63·23 of carbon and 6·13 of hydrogen). This analysis settles the true formula of brucine.

Hydroferrocyanate and Hydroferricyanate of Brucine are compounds perfectly similar to the strychnine-salts above described. The hydroferrocyanate is, according to Brandis(2), $2\,C_{46}\,H_{26}\,N_2\,O_8$, H_2 Cfy + 2 HO, or 2 ($\overset{+}{Br}$, H Cy) + FeO, H Cy + HO, when considered as a hydrocyanate.

Bromobrucine.—On treating an aqueous solution of sulphate of brucine with a weak solution of bromine in alcohol until $\frac{1}{3}$ or $\frac{1}{4}$ of the base is precipitated in form of a resinous body, and recrystallizing, from dilute alcohol, the precipitate, produced by addition of ammonia to the filtrate, Laurent(3) obtained small, slightly coloured needles, represented by the formula $C_{46}\,H_{25}\,Br\,N_2\,O_8$, (theory 16·9; experiment 17·5 per cent of bromine). These crystals are not reddened by nitric acid.

Products of Decomposition of Brucine by means of Nitric Acid.—Gerhardt(4) stated, in 1845, that in acting with nitric acid upon brucine, nitrous ether is evolved. His statement was based upon the facts: that the gas evolved possessed the same odour as nitrite of ethyl, that it was soluble in water and spirits of wine, and burned with a greenish flame, nitrous fumes being disengaged. Gerhardt inferred that brucine was resolved in this reaction precisely into nitrite of ethyl and a residual body; in the equation, however, by which he represented this reaction, a composition was assigned to this residual body, which did not agree with his own analysis. Gerhardt's statement respecting the identity of the gas evolved, with the vapour of nitrous ether, was supported by no argument based upon the

(1) Ann. Ch. Pharm. LXV, 219.
(2) Ibid. LXVI, 257.
(3) Ann. Ch. Phys. [3] XXIV, 311; Ann. Ch. Pharm. LXIX, 8.
(4) Compt. Rend. des Trav. Chim. Avril, 1845.

Products of decomposition of brucine by means of nitric acid.

well known properties of this body (boiling-point, composition, decomposition by potassa); and respecting these properties, Gerhardt entertained erroneous views. Liebig(1), who pointed out this error, confirmed the evolution from brucine, when treated with nitric acid at a gentle heat, of a gas burning with a green flame, from which, however, a liquid may be condensed, which is heavier than water (nitrous ether being lighter), and boils at 70°—75° (nitrous ether boiling at 16·5°). Gerhardt(2) replied, that the difference of the results was caused by Liebig having supported the reaction by heat, whilst nitrite of ether was only evolved in the state of purity, when there was no application of artificial heat; in repeating the experiment he again obtained a colourless gas, possessing the odour of some apples, imparting a black colour to a solution of green vitriol, and burning with greenish-white flame, from which, however, even by passing it through a frigorific mixture, only a trace of liquid could be condensed.—Laurent(3) subjected 15—20 grm. of brucine to the action of nitric acid, and passed the vapour disengaged over lime, and subsequently into a frigorific mixture; he obtained about 1 grm. of liquid, which was lighter than water, possessed the odour of apples, and could be distilled at 10° without entering into ebullition. In analysing this liquid, 29 per cent of carbon and 6·1 of hydrogen were obtained, numbers which are in the atomic proportion of 4 C : 5 H, but inferior to those representing the composition of nitrite of ethyl, (32·0 and 6·6), a deficiency which Laurent attributes to a loss in the analysis. The amount of nitrogen present Laurent assumes to be 1 eq., inasmuch as a liquid boiling at so low a temperature, (which was, however, not determined), and containing only 26 per cent of carbon and 6 of hydrogen, could not contain more than 1 eq. of nitrogen. (We here observe, that though a connexion has been pointed out between the atomic constitution of compounds and their boiling-points, no relation has as yet been established between percentage-composition and boiling-point; it is erroneous to assume that we may infer the atomic constitution from the boiling-point and then go back to the percentage; because the boiling-point may vary considerably if the equivalents are different, though the atomic constitution be the same). Laurent farther adduces, that Fournet also has obtained in this manner a liquid possessing all the properties of nitrous ether,

(1) Ann. Ch. Pharm. LVII, 94, 95.
(2) J. Pharm. [3] IX, 317.
(3) Compt. Rend. XXII, 633; Ann. Ch. Phys. [3] XXII, 463; XXIV, 314; J. Pr. Chem. XLV, 348.

Products of decomposition of brucine by means of nitric acid.

without, however, specifying to which properties the term "all" here applies. When the action of nitric acid upon brucine at the common temperature is terminated, the residuary solution deposits an orange-yellow, crystalline compound, which Laurent calls *cacotheline*, and for which he proposes the formula $C_{42} H_{22} N_4 O_{20}$; the following equation illustrates, according to Laurent, the decomposition of brucine by nitric acid, $C_{46} H_{26} N_2 O_8 + 3 (HO, NO_5) = C_{42} H_{22} N_4 O_{20} + C_4 H_5 O, NO_3 + 2 HO$. Cacotheline dissolves in aqueous ammonia with a yellow colour, which on ebullition, turns green, and afterwards brown; once this solution deposited a yellow basic compound, insoluble in alcohol and water, and containing the elements of hyponitric acid; this compound gave with hydrochloric acid, a solution, yielding with ammonia a gelatinous, with bichloride of platinum an orange-red precipitate, which, when dried at different temperatures, assumed a black or a bluish-black colour.—Rosengarten(1) found that the gas evolved when brucine is acted upon by nitric acid in the cold, after having been dried by lime and chloride of calcium, contains carbon and hydrogen in the atomic ratio 4 : 6·1 and even 4 : 6·5, which does not agree with the ratio in nitrous ether. In cacotheline he found numbers closely representing carbon and hydrogen as in Laurent's formula; the nitrogen was about 1 per cent higher. Rosengarten observed that this compound crystallizes from an aqueous solution strongly acidulated with nitric acid, in beautiful yellow plates, and that its ammoniacal solution, when mixed with nitrate of silver, yields a flocculent precipitate, detonating on exposure to heat. On distilling brucine with sulphuric acid and binoxide of manganese, the aqueous distillate was found to contain a body of peculiar odour, reducing nitrate of silver, and not altered by potassa(2).

(1) Ann. Ch. Pharm. LXV, 111; J. Pharm. [3] XIII, 232.

(2) The heavy ethereal body obtained by Liebig is a constant product of the action of boiling nitric acid on brucine, and may be condensed by a common cooling apparatus; on passing the vapour evolved in the reaction over lime and chloride of calcium, this compound may have been condensed; at all events, it differs from the substance analysed by Laurent.—Baumert found that by treating brucine with binoxide of manganese and sulphuric acid, a volatile, combustible liquid is obtained, containing two bodies, of which the one has an acid reaction and reduces silver-salts; the other, which is the combustible body, dissolves in water in all proportions; from this solution it is not separated by chloride of calcium, but by carbonate of potassa. After a first rectification over chloride of calcium, it contained 31 per cent of carbon and 12·3—12·5 of hydrogen; after a second, 33·8—33·9 of carbon and 12·3—12·5 of hydrogen. G. Merck, who appears to have obtained this body in a more anhydrous state, found, on analysis, 34·5 of carbon and 12·2 of hydrogen, and after another distillation, 37·8 of carbon and 12·4 of hydrogen, numbers agreeing with the percentage of pyroxylic spirit.—We may adduce

Theobromine.

Theobromine discovered by Woskresensky in cacao-beans, had been found, by the same chemist, to contain $C_9 H_5 N_3 O_2$; this formula remained doubtful, Woskresensky having omitted to control it by a determination of the equivalent of the base. Glasson(1), in repeating the analysis, arrived at exactly the same numbers for carbon and hydrogen as Woskresensky; he found, however, 4 per cent less of nitrogen. His results lead to the formula $C_{14} H_8 N_4 O_4$, which is confirmed by the analysis of the platinum- and of the silver-salt. From a solution of theobromine in concentrated hydrochloric acid, the compound $C_{14} H_8 N_4 O_4$, HCl is deposited in crystals, which are easily decomposed by water. At 100° the whole of the acid is evolved. The nitrate $C_{14} H_8 N_4 O_4$, HO, NO_5 is obtained in oblique rhombic prisms, on dissolving the base in gently heated nitric acid. A dilute solution of nitrate of theobromine yields with nitrate of protoxide of silver, difficultly soluble, brilliant needles, which contain $C_{14} H_8 N_4 O_4 + AgO, NO_5$. Theobromine forms with bichloride of platinum, a double-salt, crystallizing in beautiful monoclinometric prisms presenting combination-planes of ∞ P . 0 P. It contains 8·53 per cent = 4 eq. of water, and is, when dried at 100°, represented by the formula $C_{14} H_8 N_4 O_4$, HCl, $Pt Cl_2$.

Glasson's experiments show that the oxygenated bases form a series similar to those of various volatile bases, free from oxygen, and of the acids represented by the formula $C_n H_n O_4$.



$$\underbrace{C_{14} H_8 N_4 O_4}_{\text{Theobromine.}} = \underbrace{C_{16} H_{10} N_4 O_4}_{\text{Caffeine.}} - C_2 H_2.$$

Both bases exhibit the same deportment with oxidizing agents. When carefully oxidized, by binoxide of lead and sulphuric acid, theobromine yields a weakly acid substance, imparting a purple-red colour to the skin, and decomposing hydrosulphuric acid, with deposition of sulphur. Many organic bases, as is well known, when acted on by powerful oxidizing agents, give rise to the formation of splendidly coloured compounds; researches in this direction promise results of great importance respecting our ideas of the constitution of this remarkable class of bodies.

here, that leucine, which presents some analogy with the organic bases, on distillation with sulphuric acid and binoxide of manganese, yields a volatile combustible liquid, which is valeronitrile; when distilled with binoxide of lead, leucine yields at first butyraldehyde, and lastly ammonia, forming in the distillate crystals of butyraldehyde-ammonia.

(1) Ann. Ch. Pharm. LXI, 335; J. Pr. Chem. XLI, 92.

Caffeine.—In consequence of Payen's(1) statement, that caffeine contains $C_{16}H_{10}N_4O_3$, Nicholson(2) has repeated the analysis of this base, and of its platinum-compound. His results confirm, as was to be expected, the formula $C_{16}H_{10}N_4O_4$ which had been established by the well-concordant experiments of Liebig and Pfaff, Wöhler, Mulder, and Stenhouse. Incidentally to his experiments, Nicholson has examined several new caffeine double salts.—*Nitrate of protoxide of silver-caffeine*, $C_{16}H_{10}N_4O_4$, AgO, NO_5, crystallizes in white hemispheres, which are deposited on the sides of the vessel, on adding an excess of nitrate of protoxide of silver to a concentrated aqueous, or to an alcoholic solution of caffeine.—*Caffeine-protochloride of mercury*, $C_{16}H_{10}N_4O_4$, 2 Hg Cl, forms needles resembling the base, which are readily soluble in water, alcohol, hydrochloric, and oxalic acids, but almost insoluble in ether.—*Caffeine-gold-salt*, $C_{16}H_{10}N_4O_4$, HCl, Au Cl_3, is obtained as a beautiful lemon-yellow crystalline precipitate, on adding an excess of terchloride of gold to a concentrated solution of caffeine in hydrochloric acid. When washed with water, and dissolved in alcohol, it deposits long orange-yellow needles. When heated, the solution is decomposed, with separation of metallic gold.—Caffeine combines also with cyanide of mercury, and protochloride of palladium.

According to Rochleder(3) caffeine contains part of its carbon and nitrogen in the form of cyanogen; when boiled with polysulphide of ammonium, it yields a liquid, giving with sesquichloride of iron, a transient reaction of hydrosulphocyanic acid; when heated with soda-lime to 180°, together with carbonic acid and ammonia large quantities of cyanide of potassium are produced. A similar deportment is not exhibited by piperine, morphine, quinine, and cinchonine. On ebullition with chlorate of potassa and hydrochloric acid, caffeine is converted into a new body of a peculiar odour, whose solution reddens the skin, and assumes with the alkalies, and with salts of protoxide of iron an indigo-blue colour. Similar phenomena had been observed previously by Stenhouse when oxidizing caffeine with nitric acid, and by Glasson when treating theobromine with binoxide of lead and sulphuric acid.—Bichloride of platinum and caffeine yields on ebullition with dilute nitric acid a new double salt, crystallizing in six-sided tables.

(1) J. Pr. Chem. XXXVIII, 437; Berzelius' Jahresber. XXVII, 339.
(2) Ann. Ch. Pharm. LXII, 71; J. Pr. Chem. XLI, 457; Phil. Mag. [3] XXXI, 115; Chem. Soc. Mem. III, 321: J. Pharm. [3] XII, 293.
(3) Ann. Ch. Pharm. LXIII, 201.

Berberine.

Berberine.—Bödeker(1) has proved that the colombo-root of pharmaceutists, contains together with columbine and columbic acid a considerable quantity of berberine, combined with the latter acid. It is deposited in the yellow layers of the cellular membranes, mixed with a fatty substance, while columbine exists in the crystalline state in the cells of the root. Bödeker's analyses confirm the formula $C_{42}\ H_{18}\ N\ O_{9}$, proposed for berberine by Fleitmann. Berberine, when distilled with milk of lime or with hydrated protoxide of lead yields chinoline.

G. Kemp(2) recalls the fact, that as far back as 1839, therefore before Fleitmann, he has pointed out the faculty possessed by berberine, of combining with acids; he believes that Fleitmann's formula is incorrect, and proposes on the ground of the analysis of the platinum-salt (experiment 46·23 of carbon, 3·68 of hydrogen, and 18·05 of platinum) the formula $C_{42}\ H_{17}\ N\ O_{7}$. It was, however, proved by Bödeker, that the platinum-salt, when carefully prepared, yields the proper percentage (17·53) of platinum.

Harmaline.—Fritzsche(3) has published a comprehensive investigation of harmaline and harmine, two organic bases, contained ready formed in the seeds of *Peganum Harmala*, the former of which, discovered by Göbel in 1837, had been subjected to analysis by Varrentrapp and Will. Both bases occur in the shell of the seed and in the membrane just underneath it, while the interior nucleus is almost free. They are obtained by the following process: the seeds are finely powdered, and exhausted with water containing sulphuric or acetic acid; on nearly saturating the coloured extract with carbonate of soda, and adding chloride of sodium, the bases are perfectly precipitated in the form of hydrochlorates, the filtrate yielding scarcely a farther trace on addition of potassa. The precipitated hydrochlorates, which are still coloured, are washed with a concentrated solution of chloride of sodium, dissolved in water, and decolourized by animal charcoal; the yellow filtrate is heated to 50—60°, and gradually mixed with ammonia, the liquid being continually and strongly stirred, when first harmine is precipitated, which under the microscope appears in needles, whilst harmaline forms plates. On carefully adding ammonia an accurate

(1) Ann. Ch. Pharm. LXVI, 384; LXIX, 37; J. Pr. Chem. XLIII, 501; Instit. 1848, 193.

(2) Chem. Gaz. 1847, 209.

(3) Petersb. Acad. Bull. VI, 49; J. Pr. Chem. XLI, 31; XLII, 275; Ann. Ch. Pharm. LXIV, 360; J. Pharm. [3] XIII, 373.

separation is effected; finally, the harmaline is precipitated by an excess of ammonia. Fritzsche obtained from the seed nearly 4 per cent of bases, of which $\frac{2}{3}$ were harmaline. The crude harmaline is purified by suspending it in water, adding, drop by drop, acetic acid, until the larger portion is dissolved, and precipitating the dilute filtrate by means of nitrate of soda, chloride of sodium or hydrochloric acid; the harmaline-salt thus produced, after having been washed with a dilute solution of the precipitant, is dissolved in hot water, digested with animal charcoal, until the solution appears of a pure sulphur-yellow, and, while still hot, it is precipitated by an excess of potassa. If the bases be still coloured, the whole operation or part of it, has to be repeated. On filtering and washing, harmaline assumes usually a brownish colour, which occurs even more readily if ammonia has been used as the precipitant. The base forms leaf-like expanded, scaly crystals, of nacreous lustre, which are the larger, the slower the precipitation took place. If air be carefully excluded, harmaline is deposited from alcohol in large colourless crystals, whose form, according to Nordenskiöld's(1) determination is a rhombic pyramid P with $\infty \breve{P} \infty$, $\infty \bar{P} \infty$ and $\bar{P} \infty$. The ratio of the principal and both lateral axes is 1:1·804:1·415; the angles of the terminal edges at P are 116°34′ and 131°18′, the angle of the lateral edges is 83°54′. Harmaline.

Harmaline is difficultly soluble in water, and nearly tasteless; the salts have a purely bitter taste. It dissolves slightly in cold, and readily in boiling alcohol, ether dissolves so little, that alcoholic solutions are precipitated by ether. Harmaline, when heated with ammonial salts, liberates the ammonia. In analysing this base, and several of its salts, Fritzsche obtained results, which can be reconciled only with the formula $C_{27} H_{14} N_2 O_2$ (theory 73·6 of carbon, 6·34 of hydrogen, and 12·7 of nitrogen; experiment 73·15—73·92 of carbon, 6·52—6·70 of hydrogen, and 12·33 of nitrogen). This formula is supported by the analysis of harmine, and the bases produced from harmaline by the action of nitric and hydrocyanic acids, which will be mentioned hereafter; still it is suspicious on account of the odd number of carbon-equivalents; which, as in the case of berberine, closely allied with harmaline, may probably be raised to a number divisible by 14, namely, to 28, if the determination of the carbon be again carefully repeated.

The salts of harmaline are of a pure sulphur-yellow; even the

(1) Petersb. Acad. Bull. VI, 58.

Harmaline. purest base yields yellow solutions, which impart a yellow colour to cloth mordantized with alum; this colour, however, is so feeble, and of so little stability, that harmaline cannot be classed among the colouring matters.

Hydrochlorate of harmaline, $C_{27} H_{14} N_2 O_2$, $HCl + 4 HO$, is best prepared by precipitating the acetate with an excess of hydrochloric acid, and washing the precipitate with the acid in a dilute state; it forms delicate yellow needles, containing 12·30 per cent (4 equivs.) of water of crystallization, and is readily soluble in water and alcohol. —*Hydriodate* and *hydrobromate of harmaline* resemble the preceding salt.—The *platinum-salt* is yellow and crystalline, and contains $C_{27} H_{14} N_2 O_2$, HCl, $PtCl_2$ (theory 38·07 of carbon, 3·51 of hydrogen, and 23·12 of platinum; experiment 37·62 of carbon, 3·54 of hydrogen, and 23·27 of platinum).—Harmaline produces a crystalline compound also with protochloride of mercury.—Of the numerous salts described by Fritzsche, we mention the two combinations with chromic acid. The *neutral chromate* is formed by saturating a solution of acetate of harmaline with solid neutral chromate of potassa, when the neutral chromate of harmaline is separated after some time in form of a yellow thick liquid which is soluble in water, and gradually becomes crystalline and insoluble when left to itself. *Bichromate of harmaline*, $C_{27} H_{14} N_2 O_4$, HO, $2 CrO_3$, is precipitated in orange-red tufts of crystals, directly upon adding chromic acid or bichromate of potassa to a solution of the base. The precipitation is nearly complete. When heated above 120° it is decomposed into harmine, which sublimes, and a residue containing sesquioxide of chromium.—There exists a sulphate and a bisulphate of harmaline; both are crystalline; the sulphite forms a yellow varnish; the hydroferrocyanate is a brick-red powder; the hydroferricyanate crystallizes in greenish-brown prisms, the hydrosulphocyanate, nitrate and phosphate in yellow needles. Hydrosulphate and carbonate of harmaline (deposited in the crystalline form, the former, by adding to the acetate sulphide of ammonium, the latter, by decomposing the acetate with bicarbonate of soda) are readily decomposed. Acetate of harmaline crystallizes only with difficulty; when heated it loses the acid.

Harmine. — *Harmine*(1), (formerly called leucoharmine by Fritzsche), as stated above, is ready formed in harmala-seed, together with harmaline, and may be artificially prepared from the latter. On heating chromate of harmaline to 120° in a capacious flask, air being as carefully as possible excluded, a sudden decomposition takes place

(1) Petersb. Acad. Bull. VI, 242.

in the whole mass, harmine being formed, part of which sublimes. The residue (amounting to 65 per cent) yields to alcohol or water, acidulated with hydrochloric acid the new base (about 25 per cent of the harmaline-salt employed), which may be precipitated from the acid solution by an alkali. Harmine is obtained in larger quantity by heating nitrate of harmaline with a mixture of alcohol and hydrochloric acid, until ebullition ensues by the action of the acid on the alcohol. On rapidly cooling, hydrochlorate of harmine is precipitated, which is dissolved in water, and precipitated by an alkali. The crude harmine, containing harmaline, is dissolved in alcohol and a sufficient amount of hydrochloric or acetic acid; the solution is digested with animal charcoal, and, while still hot, precipitated with a sufficient quantity of ammonia. On rapidly cooling, harmine separates first in crystals, from which the mother-liquor has to be decanted directly.—Harmine forms colourless, very brittle crystals, very brilliant and powerfully refractive of light; their form is a rhombic prism of 124°18′ and 55°42′. It exhibits the same solubility as harmaline, but is less basic; its salts are colourless, and of a purely bitter taste, when mixed with an alkali, they yield oily droplets, which gradually become crystalline, just as in the case of the harmaline-salts. Fritzsche proposes the formula $C_{27}H_{12}N_2O_2$ for this base; (theory 74·35 of carbon, 5·49 of hydrogen, and 12·83 of nitrogen; 5 experiments gave 73·89—74·61 of carbon, 5·32—5·77 of hydrogen, and 13·02 of nitrogen). Hence the conversion of harmaline into harmine is due to the elimination of 2 equivs. of water. Harmine.

Hydrochlorate of harmine, $C_{27}H_{12}N_2O_2$, HCl + 4 HO, separates, nearly completely, on addition of an excess of dilute hydrochloric acid to a solution of the base in this acid. It forms delicate needles, containing, when dried in the air, 12·38 per cent (4 equivs.) of water; from strong alcohol it crystallizes without water.—The *platinum-salt* contains, according to Fritzsche's analysis, 37·90 of carbon, 3·17 of hydrogen, and 23·25 of platinum; the formula, $C_{27}H_{12}N_2O_2$, HCl, $PtCl_2$, requires, 38·25 of carbon, 3·06 of hydrogen, and 23·23 of platinum.—Both the neutral sulphate, $C_{27}H_{12}N_2O_2$, SO_3 + 2 HO, the bisulphate, $C_{27}H_{12}N_2O_2$, 2 (HO, SO_3), and the binoxalate, $C_{27}H_{12}N_2O_2$, 2 (HO, C_2O_3), form needle-shaped crystals. The solution of acetate of harmine is decomposed, on evaporation, with separation of the base; the bichromate, $C_{27}H_{12}N_2O_2$, HO, 2 CrO_3, when heated, exhibits a deportment similar to that of the harmaline-salt, a new base being produced, which has not, as yet, been farther examined. Combinations with carbonic and hydrosulphuric acids, could not be obtained.

Hydrocyanoharmaline.

Hydrocyanoharmaline.—Harmaline has a remarkable tendency to combine with hydrocyanic acid, a substance being produced which cannot be considered as a hydrocyanate, inasmuch as it is decomposed neither by alkalies, nor by strong acids, but possesses the properties of an organic base. Fritzsche calls this substance *hydrocyanoharmaline*(1). It is prepared by dissolving harmaline in a dilute alcoholic solution of hydrocyanic acid, or by adding hydrocyanic acid to the acetate, or more rapidly, by decomposing a harmaline-salt with cyanide of potassium. From an aqueous solution this compound is precipitated in the amorphous, from an alcoholic solution, in the crystalline state; an admixture of harmaline may be removed by dilute acetic acid. Hydrocyanoharmaline crystallizes in thin rhombic plates, which are not altered in the air; at 180°, or by ebullition with water or alcohol, they are completely decomposed into hydrocyanic acid and harmaline. Analysis led to the formula, $C_{29} H_{15} N_3 O_2 = C_{27} H_{14} N_2 O_2$, HCy (theory 70·68 of carbon, and 6·05 of hydrogen; experiment 69·81 of carbon, and 6·49 of hydrogen). Hence it contains 10·92 per cent of hydrocyanic acid (experiment 10·96).

Hydrocyanoharmaline saturates the same amount of acid as the harmaline contained therein; its salts, which are colourless, are formed by directly acting with the acids on the compound; they are readily decomposed by drying and keeping into hydrocyanic acid and yellow salts of harmaline; this decomposition ensues even, if dilute solutions be employed in preparing the compound. Hydrochlorate of hydrocyanoharmaline, $C_{29} H_{15} N_3 O_2$, HCl, forms microscopic rhombic octohedrons, with secondary planes (theory, 12·85; experiment, 12·86 of hydrochloric acid). When heated with an excess of nitric acid, hydrocyanoharmaline is converted, with evolution of nitrous fumes, into a purple-red liquid, which, on cooling, deposits a powder of the same colour, but very unstable, and turning green when treated with ammonia. Together with this red compound other substances are produced, which Fritzsche has not as yet examined.

Nitroharmaline.—This base, which Fritzsche described formerly under the name chrysoharmine, is obtained by the action of an excess of nitric acid upon harmaline, which loses 1 equiv. of hydrogen, and assimilates 1 equiv. of hyponitric acid(2). Fritzsche

(1) Petersb. Acad. Bull VI, 289; J. Pr. Chem. XLIII, 144; J. Pharm. [3] XIV, 73; Ann. Ch. Pharm. LXVIII, 351.

(2) Petersb. Acad. Bull. VII, 129; J. Pr. Chem. XLIV, 370; Ann. Ch. Pharm. LXVIII, 355.

recommends to heat gently a solution of 1 part of harmaline in from 6 to 8 parts of alcohol of 80 per cent, with a mixture of 2 parts of sulphuric acid, and 2 parts of moderately concentrated nitric acid; after a short ebullition the liquid is rapidly cooled, when the base is separated as bisulphate. This salt is washed with alcohol, acidulated with sulphuric acid, dissolved in hot water, and decomposed by an alkali, with the precaution of adding the latter drop by drop to the cold solution, until a slight but permanent precipitate is produced, and the filtrate has assumed a pure golden-yellow colour; this is now mixed with a few drops of an acid, heated to 40° — 50°, and completely precipitated by an excess of alkali. If nitroharmaline contain an admixture of harmaline, or harmine, the mass is suspended in water, and dissolved in a saturated aqueous solution of sulphurous acid, when sulphite of nitroharmaline is rapidly deposited, which is washed with sulphurous acid, and decomposed as above directed. Nitroharmaline.

Nitroharmaline forms pale-yellow, very slender prisms, which are but slightly soluble in cold, but dissolve more readily in boiling water; its saline solutions are not completely precipitated by the alkalies. It is easily soluble in alcohol, and both ethereal and fatty oils, but only slightly so in ether; a cold saturated alcoholic solution of the base is not precipitated by ether. At the boiling temperature, nitroharmaline decomposes the salts of ammonia. In four analyses of this compound, Fritzsche obtained 60·37 — 61·84 of carbon, 5·01 — 5·22 of hydrogen, and 14·61 — 16·24 of nitrogen. On these data, and on the analysis of the hydrochlorate and the platinum-salt, he calculates the formula $C_{27} H_{13} N_3 O_6$, which requires 61·17 of carbon, 4·89 of hydrogen, and 15·83 of nitrogen.

Hydrochlorate of nitroharmaline, $C_{27} H_{13} N_3 O_6$, HCl (theory, 12·08; experiment, 12·14 of hydrochloric acid), is obtained by adding hydrochloric acid to an alcoholic solution of the base, or to an aqueous one of the acetate; it forms yellow, slender prisms.—The *platinum-salt* is a pale-yellow, flocculent precipitate, which gradually becomes darker and crystalline; it contains $C_{27} H_{13} N_3 O_6$, HCl, $Pt Cl_2$ (theory, 34·43 of carbon, 2·96 of hydrogen, and 20·91 of platinum; experiment, 34·21 of carbon, 3·08 of hydrogen, and 21·09 of platinum).—There exists a *neutral sulphate*, and a *bisulphate of nitroharmaline*; they are both yellow and crystalline, the former easily, the latter but slightly soluble in cold water; the bisulphate has the formula $C_{27} H_{13} N_3 O_6$, 2 (HO, SO_3), (theory 22·04, experiment 21·98 of sulphuric acid). Fritzsche mentions, moreover, compounds of nitroharmaline with protochloride of

Nitroharmaline. mercury, with hydriodic, hydrobromic, hydroferro-, hydroferri-, and hydrosulphocyanic acids, with sulphurous, nitric, carbonic, oxalic, acetic, and chromic acids. The carbonate exists only in solution; the oxalate and acetate are both very soluble. Nitroharmaline exhibits the same deportment with hydrocyanic acid as harmaline, a new compound being produced, which has not yet been more minutely examined.

Corydaline.—In subjecting this body to a new analysis, Ruickholdt(1) has obtained results differing from those of Fr. Döbereiner. He found 60·19 of carbon, 5·89 of hydrogen, 3·01 of nitrogen, and 30·89 of oxygen; the formula $C_{45} H_{27} N O_{18}$, however, which he deduces from these results deserves no confidence. Wackenroder(2) states that hydrochlorate of corydaline crystallizes in right rhombic prisms, with right six-sided terminal planes; they are yellowish-green, brittle, and of a penetrating bitter taste. It dissolves in water and alcohol, and yields, with ammonia, white flakes of corydaline; the base is easily soluble in an excess of soda. Hydrochlorate of corydaline loses, according to Wackenroder, at 100°, 12·5 per cent, at 170°, 3·01 per cent more of water, and contains 10·78 per cent of hydrochloric acid; upon these data, Wackenroder calculates the formula $C_{50} H_{30} N O_{20}$, 2 HCl + 12 HO, which likewise requires additional experimental evidence.—Ruickholdt, in preparing the base from the tubers of *Corydalis tuberosa*, used a method, not essentially differing from that of Wackenroder(3), and by which corydaline appears to be partially converted into the amorphous state.

Digitaline.—Walz(4) recommends the following method of preparing digitaline, as the most appropriate. The alcoholic extract of the dry plant (prepared with eight times its weight of spirits of wine, of the spec. grav. 0·852) is treated with water, as long as it yields to it a bitter taste. The aqueous solution thus obtained is digested with levigated protoxide, and mixed with tribasic acetate of lead, until the latter ceases to produce a farther precipitate; the filtrate is then freed from lead by sulphuric acid, neutralized with ammonia, and the digitaline is precipitated by means of tannin. It is washed and triturated either with freshly precipitated protoxide of lead, or with a mixture of the common protoxide and the tribasic

(1) Arch. Pharm. [2] XLIX, 139; Ann. Ch. Pharm. LXIV, 369.
(2) Ibid. [2] XLIX, 153.
(3) Kastn. Arch. VII, 417; Berzelius' Jahresber. VII, 220.
(4) Jahrb. Pr. Pharm. XIV, 20.

acetate, and repeatedly exhausted with alcohol. The extract, when treated with hydrosulphuric acid, and gently evaporated, deposits the base as a crystalline, yellowish-white mass.—In order to save alcohol, the aqueous decoction of the plant may be treated in the same manner as the aqueous solution of the alcoholic extract. Digitaline

Gratioline.—By subjecting *Gratiola officinalis* to the process indicated for digitaline, Walz(1) obtained a substance very similar to the latter compound, which he terms gratioline.

Agrostemmine.—By exhausting the seed of *Agrostemma Githago* with dilute spirits, containing acetic acid, boiling the tincture, when freed from alcohol, with magnesia, and treating the precipitate, thus obtained, with alcohol, Schulze(2) obtained yellowish-white fusible plates, difficultly soluble in water, but more readily so in alcohol. The solutions of this substance, which presents all the characters of an organic base, have an alkaline reaction. Agrostemmine, the peculiarity of which has still to be decided by elementary analysis, occurs, according to Schulze, principally in the seed-vessel of the plant.

Organic Bases containing Phosphorus.—P. Thenard has made the following additions(3) to his former preliminary communications(4), respecting the compounds formed, at a high temperature, by the action of chloride of methyl on phosphide of calcium. This process gives rise to the production of five new phosphorus-bodies, two of which are solids, while the remainder are liquids. One of the latter is a powerful organic base, $C_6 H_9 P$, which, by oxidation, is converted into an acid; the other is a colourless, transparent, syrupy liquid, insoluble in water, and of a very disagreeable odour. This compound which contains $C_4 H_6 P$, boils at 250°; it is self-inflammable; when exposed, however, to the gradual action of oxygen, it is transformed into a crystalline acid. When treated with hydrochloric acid gas, it yields first a stable crystalline salt, and subsequently an acid liquid compound of less stability: the last products of the action of hydrochloric acid are the hydrochlorate of the base $C_6 H_9 P$, and a yellow body $C_2 H_3 P_2$, which is tasteless and inodorous.—The crystalline hydrochlorate of the compound $C_4 H_6 P$ is soluble, without decomposition, in water at 0. When gently heated, however, it assimilates the elements of water, and yields the same

(1) Jahrb. Pr. Pharm. XIV, 22.
(2) Arch. Pharm. [2] LV, 298; LVI, 163; Ann. Ch. Pharm. LXVIII, 350.
(3) Compt. Rend. XXV, 892; Phil. Mag. [3] XXXII, 153.
(4) From Instit. 1846, Nr. 602 in Berzelius' Jahresber. XXVI, 598.

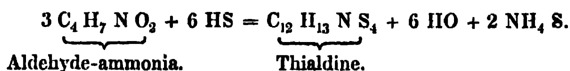
Organic bases containing phosphorus.

acid which arises from the base $C_6 H_9 P$, and a new gas $C_2 H_5 P = C_2 H_2, PH_3$; the latter combines with an equal volume of oxygen, and is converted into a very acid liquid; with 1 or 2 vols. of hydrochloric acid gas it is condensed into a crystalline compound, from which the new gas is liberated again on addition of water. P. Thenard considers these most remarkable bodies to be compounds of the three hydrides of phosphorus, $P_2 H$, PH_2 and PH_3, with 1, 2, or 3 equivs. of methylene, $C_2 H_2$. Hence, the base is $PH_3, 3 C_2 H_2$, the self-inflammable body, $PH_2, 2 C_2 H_2$, and the yellow compound, $P_2 H, C_2 H_2$. Thenard mentions, moreover, that a series of similar bodies is produced, by the action of chloride of ethyl upon phosphide of calcium. The interest excited by these compounds, is still raised by the discovery lately (1849) made by Wurtz(1), that ammonia yields analogous bases with methyl and ethyl, confirming, in a beautiful manner, a conjecture previously enunciated by Thenard.

Thialdine.—By passing hydrosulphuric acid gas through a solution of aldehyde-ammonia (free from alcohol and ether), in from 12 — 15 parts of water, containing for every ounce of liquid about ten or fifteen drops of ammonia-solution, Liebig and Wöhler(2) obtained large, camphor-like crystals of a new organic base, free from oxygen, but containing sulphur, which they designate by the name *thialdine* (contracted from θεῖον, sulphur, and aldehyde). The crystals, which are completely deposited after four or five hours, are collected on a funnel, freed from sulphide of ammonium by washing with water, and dried between bibulous paper. Their solution in ether containing $\frac{1}{3}$ of its bulk of alcohol, when slowly evaporated, yields regular rhombic tables of considerable size.—It happens, sometimes, that instead of the crystals, a colourless heavy oil, of a most offensive odour, is produced; in this case, the oil is allowed to subside, and after the separation of the aqueous layer it is agitated with $\frac{1}{2}$ vol. of ether, in which it dissolves forthwith. This ethereal solution is mixed with a little hydrochloric acid, in a well-corked flask; a magma of crystals of hydrochlorate of thialdine is at once produced, which is collected upon a filter, and separated from adhering oil by means of ether. The base itself is finally obtained by wetting the dry hydrochlorate with concentrated ammonia, and dissolving the thialdine in ether. It is then crystallized in the above manner.—Thialdine is obtained in colourless transparent

(1) Compt. Rend. XXVIII, 223.
(2) Ann. Ch. Pharm. LXI, 1; Phil. Mag. [3] XXX, 470; Chem. Soc. Mem. III, 303; J. Pharm. [3] XI, 398.

brilliant crystals, of the form of gypsum, powerfully refracting light, and possessing a peculiar aromatic, and after some time, disagreeable odour. They fuse at 43°, and solidify at 42°, with crystalline structure; they evaporate even at the common temperature, and may be volatilized with water, but like aldehyde-ammonia, cannot be distilled alone without decomposition.—Thialdine is but slightly soluble in water, but dissolves readily in alcohol and ether; when powdered, it liquefies in ether-vapour. Thialdine is without alkaline reaction; it contains $C_{12}H_{13}NS_4$.—The formation of thialdine is represented by the following equation: Thialdine.



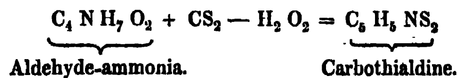
$$3\underbrace{C_4H_7NO_2}_{\text{Aldehyde-ammonia.}} + 6HS = \underbrace{C_{12}H_{13}NS_4}_{\text{Thialdine.}} + 6HO + 2NH_4S.$$

According to Wöhler and Liebig, it may be considered as a conjugate compound of 1 equiv. of NH_4S, with $3C_4H_3S$, *i. e.* with 3 equivs. of a sulphide corresponding to oxide of acetyl.—The compounds of this base, with acids, are readily crystallizable, soluble in alcohol, and insoluble in ether. When heated with nitrate of protoxide of silver, they are decomposed like thialdine itself,protosulphide of silver being precipitated, and aldehyde evolved.—Protocyanide of mercury yields, with thialdine, a white precipitate, which, on ebullition, is converted into amorphous protosulphide of mercury. On performing this reaction in a retort, a fine sublimate is formed, consisting of delicate needles, which are insoluble in water, but dissolve in alcohol and ether: this substance is not yet sufficiently examined, it appears to be thialdine, in which part, or the whole of the sulphur is replaced by cyanogen.—When heated with hydrate of lime, thialdine yields leucoline.—*Hydrochlorate of thialdine,* $C_{12}H_{13}NS_4$, HCl. A saturated solution of the base in dilute acid yields, on evaporation, colourless transparent brilliant prisms, frequently of an inch in length, which turn brown on heating, with evolution of an offensive gas, chloride of ammonium being sublimed.—*Nitrate of thialdine,* $C_{12}H_{13}NS_4$, HO, NO_5. It is best prepared by agitating an ethereal solution of impure thialdine with moderately strong nitric acid, washing with ether the crystalline magma produced, and recrystallizing from water. It forms delicate white needles, very soluble in water, but insoluble in ether.—If crystallized thialdine be left for some time in contact with sulphide of ammonium, a heavy oleaginous body is produced, which is not miscible with water; the same body is frequently obtained in preparing thialdine. This substance, as well as the cyanogen-product above-mentioned, deserve a more minute examination.

Selenal-dine.

Selenaldine.—By passing into aldehyde-ammonia a current of hydroselenic acid (disengaged from selenide of iron by dilute sulphuric acid, in an air-tight apparatus), Liebig and Wöhler obtained crystals of *selenaldine,* apparently isomorphous with thialdine, but of so little stability that they could not be subjected to analysis. It has a feeble, but disagreeable odour, and assumes at once a yellow colour, when exposed to the air; its solution, too, deposits, in contact with air, immediately, an orange-yellow amorphous body, insoluble in alcohol and ether, and fusible in hot water. They did not succeed in preparing *telluraldine.*

Carbothialdine.—According to Liebig and Redtenbacher(1), if bisulphide of carbon be added to an alcoholic solution of aldehyde-ammonia, brilliant white crystals of a new base are deposited, after some minutes, for which they propose the name *carbothialdine.* It is insoluble in water and cold ether, but dissolves readily in boiling alcohol, from which it crystallizes without alteration. It is likewise soluble, without decomposition, in dilute hydrochloric acid; the solution solidifies, after some time, to a yellowish-white magma, insoluble in water; when boiled with hydrochloric acid, carbothialdine yields chloride of ammonium, bisulphide of carbon, and aldehyde. On adding to a hot alcoholic solution of carbothialdine, oxalic acid and subsequently ether, oxalate of ammonia is separated in crystals; silver-salts produce a greenish-black precipitate, which is rapidly converted into protosulphide of silver; with protochloride of mercury and copper-salts, precipitates, respectively yellowish-white and green, are formed. Analysis led to the formula $C_5\,H_5\,N\,S_2$, which may, perhaps, be doubled or quadrupled by a determination of the equivalent, which is still wanting. The formation of carbothialdine is represented by the following equation:



$$\underbrace{C_4\,N\,H_7\,O_2}_{\text{Aldehyde-ammonia.}} + CS_2 - H_2\,O_2 = \underbrace{C_5\,H_5\,NS_2}_{\text{Carbothialdine.}}$$

Cyanethine.—According to Frankland and Kolbe(2) cyanide of ethyl, as mentioned under that head, when acted on by potassium yields a gas presenting the composition and condensation of methyl, $C_2\,H_3$, a viscid yellowish residue being left, which should contain carbon, hydrogen and cyanogen in the relation expressed by the formula $C_2\,H_2\,Cy$. Cold water extracts from this residue a considerable quantity of cyanide of potassium, a white body remaining,

(1) Ann. Ch. Pharm. LXV, 43. (2) Ibid. 269; Chem. Soc. Qu. J. I, 60.

which crystallizes from a boiling aqueous solution in nacreous plates, presenting the properties of an organic base for which Frankland and Kolbe propose the name *cyanethine*.—Cyanethine is white, inodorous and tasteless; it fuses at 190°, boils at 280°, with partial decomposition, and dissolves readily in alcohol, but only slightly in cold water. It has a feebly alkaline reaction; ebullition with potassa-solution, or fusion with the hydrate, have scarcely any effect upon it. Analysis led to the formula $C_{18}H_{15}N_3$, showing that it has the same composition as cyanide of ethyl, but the triple equivalent. Cyanethine is readily soluble in acids, giving rise to the formation of salts soluble in water and alcohol, which have an astringent bitter taste; from these salts, part of which crystallize with remarkable beauty, the base is precipitated both by caustic and carbonated alkalies.—*Nitrate of cyanethine* $C_{18}H_{15}N_3, HO, NO_5$ is neutral; it crystallizes in large colourless crystals; the sulphate and hydrochlorate are uncrystallizable. The platinum-double salt $C_{18}H_{15}N_3, HCl, PtCl_2$, crystallizes from water in large ruby-red octohedrons, which are pretty soluble in alcohol, and in a mixture of the latter with ether. The conditions which occasion the transformation of cyanide of ethyl into cyanethine have not been discovered by Frankland and Kolbe; it is formed in small quantity (only a small percentage of the cyanide of ethyl employed), by adding the cyanide, drop by drop, to potassium; by operating in the reverse manner, no cyanethine is obtained. Cyanide of ethyl is not changed when exposed with dry cyanide of potassium to a temperature of 240° in a sealed tube. Cyanethine.

Organic Bases in 'Oleum Animale Dippelii.'—Anderson (1) has published an investigation of the organic bases contained in the products of distillation of animal matters. As material he used oil of marrow, obtained in the preparation of bone-black, and consisting chiefly of the products of decomposition of gelatine, inasmuch as the bones previously to their distillation in iron cylinders are boiled with large quantities of water, in order to separate the fat. The crude commercial oil is dark-brown, nearly black, and of a spec. grav. 0·970. It yields its basic constituents to acids, which, when employed in the concentrated state and in excess, dissolve also a non-basic oil which is readily decomposed; by the alkalies an acid oil is extracted, and a pretty considerable quantity of hydrocyanic acid. Fir-wood moistened with hydrochloric acid, when exposed to the vapour of the crude

(1) Trans. Royal Soc. of Edinb. XVI, 4; Phil. Mag. [3] XXXIII, 174; Ann. Ch. Pharm. LXXX, 32; J. Pr. Chem. XLV, 153; J. Pharm. [3] XIV, 372.

Organic bases in *Oleum animale Dippelii.*

oil, rapidly assumes the purple-red colouration characterizing pyrrole. By subjecting the oil in portions of about 15lbs. to fractional distillation, in half-filled iron retorts, at first an aqueous liquid is obtained, containing ammonia and volatile bases, while at the same time a yellow oil passes over. The last three-fifths of the distillate become darker, and less fluid in proportion as the boiling-point rises; the last portion exhibits a transitory dark reddish-brown colour in transmitted, a green colour in reflected light, and becomes rapidly opaque. All the distillates contain basic bodies, about $\frac{3}{4}$ per cent of the crude oil consists of more volatile and from 2 to 3 per cent of less volatile bases. Anderson first describes the separation of the bases in the more volatile portion of the distillate. This liquid is left in contact with sulphuric acid containing 10 parts of water for eight days or a fortnight; more water is then added and decanted; this treatment is repeated until basic bodies cease to be dissolved. The red or dark-brown liquid, which contains non-basic oils and pyrrole, is mixed with more sulphuric acid, evaporated, filtered, and distilled with an excess of alkali. The first distillate is an aqueous solution of the more volatile bases; the receiver is changed as soon as an oil passes over, which is heavier than water; the oil floating on the surface of the concentrated salt-solution in the retort contains some of the less volatile bases. On adding solid potassa to the distillate, the bases dissolved are separated, with the exception of a small quantity of those which are most volatile, and which can be obtained only by distilling with a very large excess of potassa. On submitting the mixture of bases to fractional distillation, ammonia is disengaged first; at 71° the liquid enters into ebullition, a light transparent oil passing over; from 100° the receiver is changed every 10°. In this manner considerable quantities of distillate are obtained between 132 and 137°; the thermometer then rises rapidly until another basic oil is obtained between 151 and 179°, which is only difficultly soluble in water; as soon as the distillate, when treated with hypochlorite of lime, exhibits the reaction of aniline, the receiver needs no longer to be changed, the distillate consisting almost entirely of this base.

Petinine.—Anderson first describes the base contained in the most volatile portion of the distillate; he calls it *petinine* (from πετεινός, volatile). It is obtained in a state of purity, by submitting the first portion of the distillate mixed with the small quantity, which, as mentioned above, could be obtained only by distillation with an excess of potassa, to repeated distillation. A large quantity of ammonia having been evolved, the product distilling towards 80° is petinine. It

Petinine.

is a transparent colourless liquid, powerfully refracting light, and of a pungent most disagreeable odour, recalling, when dilute, that of putrid apples. It dissolves in all proportions in water, alcohol, ether, and oils, the solutions have an acrid burning taste, and are alkaline. It boils at 79·5°; its vapour forms with hydrochloric acid gas white fumes. This substance combines with concentrated acids, with evolution of heat; it precipitates salts of sesquioxide of iron and protoxide of copper; the latter oxide dissolves with a blue colour in an excess of the base. Anderson proposes for petitine the formula $C_8 H_{10} N$ (theory 66·66 of carbon, 13·88 of hydrogen, and 19·37 of nitrogen; experiment 66·66 of carbon, and 13·92 of hydrogen). The platinum-salt is $C_8 H_{10} N, HCl, PtCl_2$ (theory 17·26 of carbon, 3·96 of hydrogen, and 35·45 of platinum; experiment 16·93 of carbon, 4·17 of hydrogen, and 35·34—35·54 and 35·51 of platinum). Gerhardt(1) considers the formula $C_8 H_{11} N$ more probable (theory 65·75 of carbon, 15·0 of hydrogen; in the platinum-salt, 17·2 of carbon, 4·3 of hydrogen, and 35·26 of platinum). The latter formula would represent the butyric acid term corresponding to the bases of the methyl- and ethyl-series, $C_2 H_3 N$ and $C_4 H_7 N$ lately discovered by Wurtz.

The salts of petinine crystallize easily, and are permanent in the air; they may be sublimed without decomposition if their acid be volatile. The neutral sulphate yields, on evaporation, a bisulphate crystallizing in leafy plates, and deliquescing in moist air; the nitrate sublimes in delicate woolly crystals, the hydrochlorate in needles. The platinum-double salt crystallizes from boiling water in golden-yellow plates, resembling protiodide of lead.—Petinine is but difficultly decomposed by nitric acid, but immediately destroyed by hypochlorite of lime, a very pungent odour being evolved; the solution remains colourless. An aqueous solution of bromine separates from solutions of petinine a heavy yellow oil insoluble in acids, hydrobromate of petinine remaining in solution.

Picoline.—In a paper published in 1846 (2), Anderson showed, that coal-gas naphtha contains, along with aniline, leucoline and pyrrole, another base isomeric with aniline, to which he gave the name *picoline*. His supposition that this compound is the chief constituent of odorine, described by Unverdorben as one of the

(1) J. Pharm. [3] XIV, 378; Laurent and Gerhardt's, Compt. Rend. des Trav. Chim. 1849, 121.

(1) Trans. of the Roy. Soc. of Edinb. XVI; Ann. Ch. Pharm. LX, 80; J. Pr. Chem. XL, 124; Berzelius' Jahresber. XXVII, 370; J. Pharm. [3] XI, 393.

Picoline. components of Dippel's oil, has been proved to be correct by a more minute examination. The fraction distilling between 132 and 137^0 is picoline $C_{12} H_7 N$. The analysis both of the base and the platinum-salt prepared from Dippel's oil, leaves no doubt in this respect.

Aniline.—Barral(1) has determined the vapour-density of aniline. He found it to be 3·210. The theoretical value of the formula $C_{12} H_7 N$, representing 4 vols. of vapour, is 3·202.

Phosphates of Aniline.—Nicholson(2) has investigated the compounds of aniline with phosphoric acid; he succeeded in obtaining the salts formed by this base with common phosphoric acid and with pyro- and metaphosphoric acid. On adding an excess of aniline to a concentrated solution of tribasic phosphoric acid, a magma of crystals is produced, which when recrystallized from boiling alcohol, yields nacreous plates, resembling thionurate of ammonia. This phosphate has a slightly acid reaction; it dissolves readily in ether and water, but is less soluble in cold alcohol; it fuses at a gentle heat, and loses aniline at 100°, when it assumes a red colour.—It has the composition $2 (C_{12} H_7 N, HO), HO, PO_5$.—If the solution of this salt be mixed with tribasic phosphoric acid until it ceases to be precipitated by chloride of barium, white needles are deposited on evaporation in the water-bath. These crystals, which are readily dissolved by ether, by alcohol, and by water, (by the latter with decomposition), are represented by the formula $(C_{12} H_7 N, HO), 2 HO, PO_5$. Nicholson did not succeed in obtaining a phosphate, containing 3 equivs. of aniline.

On adding aniline to pyrophosphoric acid, a mixture of the neutral and acid salt is precipitated, which, when redissolved in an excess of the concentrated acid, deposits white needles, assuming a red tint in the atmosphere. These crystals are the acid salt $(C_{12} H_7 N, HO)$, HO, PO_5; they are soluble in water, with a strongly acid reaction, but are insoluble in alcohol and ether.

Metaphosphate of aniline, $(C_{14} H_7 N, HO), PO_5$, is precipitated as a white gelatinous mass, on adding a large excess of either aniline itself or its alcoholic or ethereal solution to metaphosphoric acid. This compound is insoluble in alcohol and ether, but dissolves in water, with an acid reaction; when boiled for some time, it is converted into common phosphate of aniline.

(1) Ann. Ch. Phys. [3] XX, 348.
(2) Phil. Mag. [3] XXX, 10; Ann. Ch. Pharm. LIX, 213.

Aniline and Protochloride of Platinum.—According to a preliminary communication, made by Raewsky(1), aniline forms three compounds with protochloride of platinum, of which the one, of a violet colour, corresponds to the green salt of Magnus; it contains Pt Cl, C_{12} H_7 N, and is capable, like the latter, of assuming a variety of isomeric conditions. The other combination is rose-red; it has the formula Pt Cl, 2 C_{12} H_7 N, and corresponds to Reiset's ammonia-compound. A third salt, of a garnet-red colour, is the hydrochlorate of the violet compound, and contains Pt Cl, C_{12} H_7 N, H Cl. Aniline and protochloride of platinum.

Organic Bases derived from Aniline.—A. W. Hofmann has communicated a series of researches on the deportment of aniline and several analogous bases with iodine, cyanogen, and chloride of cyanogen.

Iodaniline.—Anhydrous aniline, when gradually mixed with 1½ parts of iodine, solidifies after some time to a brown crystalline mass, containing chiefly hydriodate of iodaniline along with hydriodate of aniline, free iodine, and a brown iodinated product of decomposition of aniline, which is insoluble in acids, in alkalies, and in water(2). On treating this mass with dilute hydrochloric acid (of a spec. grav. 1·11), difficultly soluble hydrochlorate of iodaniline is separated, the corresponding aniline-salt remaining in solution. It is necessary to avoid the use of concentrated hydrochloric acid, which precipitates also the aniline-salt. The hydrochlorate of iodaniline is washed with a small quantity of hydrochloric acid, and dissolved in boiling water; this solution, when decolourized with animal charcoal, yields nacreous tables, resembling benzoic acid. From the solution of this salt, the iodine-base is thrown down, on addition of ammonia, in white crystals, which may be still farther purified by dissolution in alcohol and reprecipitation by water. On evaporating the alcoholic solution in the water-bath, yellow, oily drops are separated, solidifying on cooling, with crystalline structure.

The composition of iodaniline is represented by the formula C_{12} H_6 I N. It is derived from aniline by the elimination of 1 eq. of hydrogen, for which is substituted 1 eq. of iodine. This compound resembles, in many respects, aniline; and in more, the corresponding chlorine- and bromine-base. The same vinous odour, the same pungent taste, the same solubility in alcohol, ether, pyroxylic spirit, acetone, bisulphide of carbon, fatty and ethereal oils. It is but slightly soluble in water, and heavier than this liquid; it has no

(1) Compt. Rend. XXIV, 424.

(2) Chem. Soc. Qu. J. I, 269; Ann. Ch. Pharm. LXVII, 1; Ann. Ch. Phys. [3] XXV, 230.

Iodaniline. action upon vegetal colours. It forms only prismatic crystals, while brom- and chloraniline affect the form of octohedrons. The crystals fuse at 60° and solidify at 51°; they may be distilled both alone and with water. The solutions of iodaniline impart to fir-wood and the pith of the elder-tree the same intense yellow colour as aniline, chlor- and bromaniline, but do not exhibit with hypochlorite of lime the purple-violet reaction of aniline. Solid chromic acid decomposes iodaniline without inflammation. When exposed to the air, the base turns black, iodine being liberated.

The salts of iodaniline crystallize with the same facility as those of aniline; they are less soluble and yield a precipitate of iodaniline when mixed with an aqueous solution of aniline. Iodaniline precipitates salts of alumina, but has no action on iron- and zinc-salts.—*Hydrochlorate of iodaniline*, $C_{12} H_6 I N, HCl$, crystallizes in leaves and broad thin needles, which are difficultly soluble in cold water and concentrated hydrochloric acid, insoluble in ether, but dissolve readily in alcohol. The *hydrobromate* resembles the former salt in every respect; the *hydriodate* is more soluble, and rapidly undergoes decomposition. *Sulphate of iodaniline*, $C_{12} H_6 I N, HO, SO_3$, forms brilliant scales, the solution of which is decomposed, when heated to ebullition. *Oxalate of iodaniline*, $C_{12} H_6 I N, HO, C_2 O_3$, crystallizes in flattened needles, difficultly soluble in alcohol and water, insoluble in ether. The *nitrate* crystallizes in hair-like needles; its solution is not precipitated by nitrate of protoxide of silver. The *platinum-salt*, $C_{12} H_6 I N, HCl, PtCl_2$, is an orange-yellow crystalline precipitate.—Hydrochlorate of iodaniline yields, with terchloride of gold, a scarlet precipitate which is rapidly altered.

The vapour of iodaniline is readily decomposed by potassium, iodide and cyanide of potassium being formed; it is affected neither by an aqueous, nor an alcoholic solution of potassa. With chlorine it yields trichloraniline and chlorophenisic acid, chloride of iodine being evolved. Bromine converts the iodine-base into tribromaniline; when treated with a mixture of chlorate of potassa it is, like aniline, transformed into chlorokinone (chloranile) and chlorophenisic acid. Ebullition with nitric acid, gives rise to the formation of picric acid. If salts of iodaniline be treated with an amalgam of potassium, or with metallic zinc, in the presence of a free acid, aniline is regenerated.

Cyaniline.—Aniline absorbs cyanogen-gas with evolution of heat; the solution turns gradually opaque, the odour of hydrocyanic acid becoming perceptible, and a crystalline deposit being produced. According to Hofmann, if the current of cyanogen be interrupted,

as soon as the liquid has assumed a strong odour of this gas, the crystals deposited consist chiefly of an organic base, to which he gives the name *cyaniline*(1). A cold solution of aniline, in from 5 to 6 parts of alcohol, exhibits a deportment similar to that of pure aniline; the crystalline deposit, however, being much purer, in preparing cyaniline an alcoholic solution is to be preferred to the base itself. Crude cyaniline is purified in the following manner: the crystals, after having been separated from the mother-liquor by washing with alcohol, are dissolved in dilute sulphuric acid, which leaves a small quantity of a red crystalline substance. On adding ammonia to the acid solution, cyaniline is precipitated, which has still a slightly yellowish colour, but becomes colourless after repeated crystallizations from boiling alcohol. Hofmann found this compound to be $C_{14} H_7 N_2 = Cy, C_{12} H_7 N$; this formula shows that cyaniline is formed by the direct union of aniline and cyanogen. Cyaniline.

Cyaniline crystallizes in colourless tufts, of the lustre of metallic silver, which are inodorous and tasteless; they are difficultly soluble in alcohol, ether, pyroxylic spirit, bisulphide of carbon, benzole, fatty and ethereal oils, and perfectly insoluble in water. It fuses between 210° and 220°, and sinks in water, when fused, while the crystals float upon it. When heated beyond its fusing-point it is decomposed, carbon being liberated, while aniline and cyanide of ammonium are evolved; nor is cyaniline volatile with the aid of aqueous vapour. The acid solutions of this base have no action upon fir-wood, nor does cyaniline exhibit the reactions of aniline, either with hypochlorite of lime, or chromic acid.

When in contact with acids for some time, cyaniline undergoes decomposition, the cyanogen assimilates the elements of water, and aniline is separated; hence some difficulties arise in preparing pure salts of cyaniline; they correspond in composition to those of aniline.—*Hydrochlorate of cyaniline*, $Cy, C_{12} H_7 N, HCl$, is obtained by adding fuming hydrochloric acid to an equal volume of a solution of the base in boiling dilute hydrochloric acid, when colourless crystals are deposited, which may be washed with ether. This salt is readily soluble in water and alcohol, and has a remarkably sweet taste. In solution, or when kept moist for some time, it is decomposed. The *hydrobromate*, $Cy, C_{12} H_7 N, HBr$, and *hydriodate*, are similar to the hydrochlorate; the latter is still more readily decomposed. *Nitrate of cyaniline*, $Cy, C_{12} H_7 N, HO, NO_5$, crystallizes

(1) Chem. Soc. Qu. J. I, 159; Ann. Ch. Pharm. LXVI, 129; Ann. Ch. Phys. [3] XXIV, 67; J. Pharm. [3] XIV, 305.

Cyaniline. in long needles, which are difficultly soluble in water, and forms, with nitrate of protoxide of silver, a crystalline double compound. The *platinum-salt*, $Cy, C_{12} H_7 N, H Cl, PtCl_2$, is precipitated in orange-yellow needles, soluble in water and alcohol, on adding bichloride of platinum to a boiling saturated solution of the base in pretty concentrated hydrochloric acid. It is readily decomposed into the corresponding platinum-salts of aniline and of ammonium, and other products. An alcoholic or hydrochloric solution of cyaniline, yields, with terchloride of gold, an orange-yellow double salt, $Cy, C_{12} H_7 N, HCl, AuCl_3$, whose solution in ether deposits the platinum-salt of aniline.

Nicotine and leucoline, when treated with cyanogen-gas, form brown, amorphous products of decomposition, possessing no basic properties; compounds analogous to cyaniline could not be obtained.

Melaniline.—Aniline absorbs gaseous chloride of cyanogen, as obtained by the action of chlorine on moistened cyanide of mercury; in this reaction a considerable amount of heat is evolved, the liquid assumes a dark colour, thickens and solidifies gradually into a crystalline mass(1). Chloride of cyanogen having ceased to be absorbed, even on exposure of the mass to a gentle heat, the whole is converted into a brown, transparent, resinous substance, which consists chiefly of the hydrochlorate of a new organic base, for which Hofmann proposes the name *melaniline*. In order to obtain this compound in a state of purity, the hydrochlorate is dissolved in boiling water, acidulated with hydrochloric acid. From this solution the melaniline is precipitated by potassa as an oily mass, soon solidifying with crystalline structure. After having been washed with water, it requires only to be recrystallized from a mixture of equal parts of alcohol and water. The formula of melaniline is $C_{26} H_{13} N_3 = C_{12} H_7 N, C_{12} H_6 N, Cy$. Its formation, in which 2 equivs. of aniline have been acted on by 1 equiv. of chloride of cyanogen, is represented by the following equation:



$$2 C_{12} H_7 N + C_2 N Cl = C_{26} H_{13} N_3, H Cl.$$

Aniline. Chloride of cyanogen. Hydrochlorate of melaniline.

Melaniline forms white hard crystalline plates, assuming a reddish tint when exposed to the atmosphere; they are inodorous, but possess a bitter taste. It fuses at 120°—130°, and is decomposed between 140° and 150° into aniline, which distils over, and a trans-

(1) Chem. Soc. Qu. J. I, 285; Ann. Ch. Pharm. LXVII, 129.

parent brownish mass, which remains behind. The crystals float upon water, while the fused base sinks in it. Melaniline is difficultly soluble in water, it dissolves, however, easily in alcohol, ether, pyroxylic spirit, acetone, and bisulphide of carbon, fatty and ethereal oils. It has scarcely any reaction on vegetal colours; its salts have no effect upon fir-wood, nor do they exhibit, either with chromic acid or hydrochlorate of lime, the peculiar changes which characterize aniline. Melaniline.

Melaniline forms with most acids, crystalline salts, which are colourless or slightly reddish; their solutions are very bitter, and yield, when mixed with caustic or carbonated alkalies, a precipitate of white melaniline, which rapidly crystallizes.—*Sulphate of melaniline*, $C_{26}\ H_{13}\ N_3$, HO, SO_3, forms stellated, rhombic plates, which are soluble in water, alcohol, and ether.—*Nitrate of melaniline*, $C_{26}\ H_{13}\ N_3$, HO, NO_5, forms white needles; it is so completely deposited from its hot solution, that the mother-liquor becomes scarcely turbid on addition of an alkali, whence nitric acid may be used as a reagent for this base. The nitrate is likewise soluble in alcohol, but dissolves scarcely in ether. *Binoxalate of melaniline*, $C_{26}\ H_{13}\ N_3$, 2(HO, $C_2\ O_4$), resembles the sulphate; it is difficultly soluble in water and alcohol, almost insoluble in ether; when heated, carbonic oxide and carbonic acid are evolved, while aniline passes over, along with a substance of a most penetrating odour, which is perceptible likewise in various decompositions of cyaniline; towards the end of the operation, the neck of the retort becomes coated with a radiated mass of crystals, a transparent resinous residue remaining behind. The *phosphates* are readily soluble, but crystallize only very gradually; the *hydrochlorate* is the most soluble of all melaniline-salts; it dries up into a gummy mass, becoming only very slowly crystalline. *Hydrobromate of melaniline*, $C_{26}\ H_{13}\ N_3$, H Br, crystallizes readily in stellated needles, less soluble in concentrated hydrobromic acid than in water. *Hydriodate of melaniline*, $C_{26}\ H_{13}\ N_3$, H I, separates as a yellow oil, solidifying only slowly with crystalline structure, on treating the base with concentrated hydriodic acid; it is soluble in hot water and alcohol, and is decomposed in contact with the atmosphere. *Hydrofluate of melaniline* is a crystalline salt, readily soluble in water. The *platinum-salt of melaniline*, $C_{26}\ H_{13}\ N_3$, H Cl, Pt Cl_2, is a pale-yellow crystalline precipitate, slightly soluble in hot water. The *gold-salt*, $C_{26}\ H_{13}\ N_3$, HCl, Au Cl_3, is deposited in needles, of golden lustre, or as a yellow precipitate, from a mixture of hydrochlorate of melaniline with ter-

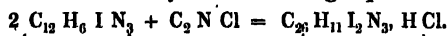
Melaniline.

chloride of gold. This salt is difficultly soluble in water, more soluble in alcohol, and dissolves readily in ether. *Nitrate of protoxide of silver-melaniline*, $AgO, NO_5, 2\,C_{26}\,H_{13}\,N_3$, is deposited from an alcoholic mixture of the base and silver-solution, in hard, white crystalline crusts. Protochloride of mercury yields with solutions of melaniline, a white compound, crystallizing in needles from acidulated water.

Metamorphoses of Melaniline. Dichloromelaniline.—Addition of an excess of chlorine-water to hydrochlorate of melaniline precipitates a resinous mass, possessing no basic properties; by interrupting, however, the treatment with chlorine-water, as soon as the resinous precipitate becomes permanent, the filtered solution yields on evaporation needle-shaped crystals, or an oil, solidifying with crystalline structure, which are the hydrochlorate of a chlorinated base, to which Hofmann assigns the name *dichloromelaniline*. The aqueous solution of this salt gives with ammonia a precipitate, which crystallizes from alcohol in hard crystalline plates. The platinum-salt of this base is an orange-yellow crystalline precipitate, which contains: $C_{26}\,H_{11}\,Cl_2\,N_3, HCl, Pt\,Cl_2$.

Dibromomelaniline.—Hydrochlorate of melaniline exhibits with bromine the same deportment. *Dibromomelaniline*, $C_{26}\,H_{11}\,Br_2\,N_3$, is almost insoluble in water, but dissolves in alcohol and ether. It has a very bitter taste. When heated beyond its fusing-point, it is decomposed into bromaniline and a resinous residue. The hydrochlorate of this base, $C_{26}\,H_{11}\,Br_2\,N_3, HCl$, is difficultly soluble in water; it crystallizes in long satiny needles; the platinum-salt, $C_{26}\,H_{11}\,Br_2\,N_3, HCl, Pt\,Cl_2$, forms scales of a golden lustre; it is almost insoluble in water.

Diodomelaniline.—This base cannot be obtained by the direct action of iodine upon melaniline; it may be prepared, however, by treating an ethereal solution of iodaniline with chloride of cyanogen. In the first stage of the process, hydrochlorate of iodaniline is deposited, which is subsequently converted into resinous, gradually crystallizing hydrochlorate of *diodomelaniline*. From the solution of this salt the base is separated by potassa; it contains $C_{26}\,H_{11}\,I_2\,N_3$; its formation is illustrated by the following equation:



$$2\,C_{12}\,H_6\,I\,N_3 + C_2\,N\,Cl = \underbrace{C_{26}\,H_{11}\,I_2\,N_3, H\,Cl.}$$

Iodaniline.	Chloride of cyanogen.	Hydrochlorate of diodomelaniline.

The double salt of diodomelaniline has the composition $C_{26}\,H_{11}\,I_2\,N_3, HCl, Pt\,Cl_2$.

Dinitromelaniline.

Dinitromelaniline.—When treated with fuming nitric acid, melaniline is converted, according to the duration of the treatment, into an orange-yellow base, or into lemon-yellow prisms of an acid forming scarlet-red salts with the alkalies. Both compounds are not yet farther investigated; however, the base produced by the action of nitric acid is not identical with the *dinitromelaniline,* which Hofmann obtained, by treating an ethereal solution of nitraniline with chloride of cyanogen. The hydrochlorate of the base, thus obtained, yields, with an alkali, brilliant, pale-yellow scales of dinitromelaniline, perfectly insoluble in water, and difficultly soluble in alcohol and ether. When heated, dinitromelaniline is decomposed, like melaniline, into a brown residue and nitraniline. Experiment led to the formula $C_{26}\ H_{11}\ (NO_4)_2\ N_3$, which was confirmed by the analysis of a difficultly soluble hydrochlorate $C_{26}\ H_{11}\ (NO_4)_2\ N_3$, HCl, and of the platinum-salt $C_{26}\ H_{11}\ (NO_4)_2\ N_3$, HCl, $PtCl_2$.

Dicyanomelaniline.—An alcoholic solution of melaniline, when saturated with cyanogen-gas, solidifies after some hours into a crystalline magma, the odour of cyanogen being replaced by that of hydrocyanic acid. After separation of the brown mother-liquor, and recrystallization from alcohol, yellow needles are obtained, which contain $C_{30}\ H_{13}\ N_5 = Cy_2,\ C_{26}\ H_{13}\ N_3$. This compound, to which Hofmann assigns the name *dicyanomelaniline,* hence arises from melaniline, similarly to cyaniline, simply by the assimilation of 2 equivs. of cyanogen. When heated dicyanomelaniline yields aniline, cyanide of ammonium, and a resinous residue. It is very soluble in dilute acids, and reprecipitable without alteration by rapidly adding an alkali; if the hydrochloric solution, however, be allowed to stand only a few minutes, a crystalline product of decomposition is deposited, which has not yet been examined; the mother-liquor contains ammonia.

Bromide of cyanogen converts aniline into hydrobromate of melaniline; iodide of cyanogen, however, gives rise to the formation of iodaniline, hydrocyanic acid being liberated.

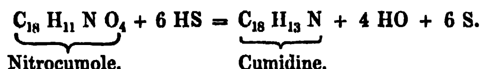
Cumidine.—E. Ch. Nicholson(1) has obtained this base from cumole in the same manner as aniline is prepared from benzole. A solution of cumole in fuming nitric acid, yields, on addition of water, nitrocumole, $C_{18}\ H_{11}\ N\ O_4$, which is dissolved in alcoholic ammonia, and repeatedly treated with hydrosulphuric acid until the last trace of nitrocumole has disappeared. Distillation of the saturated solution promotes the decomposition. The residue of the last distillation

(1) Chem. Soc. Qu. J. I, 2; Ann. Ch. Pharm. LXV, 58.

Cumidine. is treated with hydrochloric acid, which dissolves the cumidine. The solution, filtered and evaporated, yields a crystalline hydrochlorate, from which the base is separated by distillation with potassa. The distillate is converted into an oxalate, which is decolourized by animal charcoal, and recrystallized from alcohol. From this compound the pure cumidine is separated by potassa as a yellow oil.

Cumidine is a powerfully refracting liquid of a burning taste; in a freezing mixture it solidifies into square tables, it is readily soluble in alcohol, ether, pyroxylic spirit, fatty and ethereal oils, but dissolves only slightly in water; its solutions have no action on vegetal colours. The base produces an oily stain upon paper, which disappears again. Exposed to the air it turns yellow, and at last dark-red; its spec. grav. is 0·9526, the boiling-point 225°.—Cumidine precipitates the salts of sesquioxide of iron; it stains fir-wood like aniline and toluidine, but does not exhibit the peculiar reaction of aniline with hypochlorite of lime. The salts of cumidine are colourless for the greater part; they crystallize with great facility; they are soluble in water, and even more so in alcohol. They have an acid reaction, and contain no water of crystallization.

The analysis of this substance led to the formula $C_{18}\,H_{13}\,N$; its formation is illustrated by the following equation:



$$\underbrace{C_{18}\,H_{11}\,N\,O_4}_{\text{Nitrocumole.}} + 6\,HS = \underbrace{C_{18}\,H_{13}\,N}_{\text{Cumidine.}} + 4\,HO + 6\,S.$$

Nicholson has investigated the following salts of cumidine: *sulphate of cumidine* $C_{18}\,H_{13}\,N,\,HO,\,SO_3$, *nitrate of cumidine* $C_{18}\,H_{13}\,N,\,HO,\,NO_5$, *hydrochlorate of cumidine* $C_{18}\,H_{13}\,N,\,HCl$, and the *double compound with bichloride of platinum* $C_{18}\,H_{13}\,N,\,HCl,\,PtCl_2$. The latter is deposited in long yellow needles, on adding an excess of bichloride of platinum to a hot aqueous solution of hydrochlorate of cumidine. This base forms a yellow double salt with chloride of palladium, a dark-violet salt with terchloride of gold, and a salt crystallizing in needles with nitrate of protoxide of silver. An alcoholic solution of cumidine yields white precipitates with protochloride and protocyanide of mercury, and a fine green precipitate with sulphate of protoxide of copper. Potassium decomposes the vapour of cumidine with formation of cyanide of potassium; it is violently acted upon by chromic acid, but is not inflamed. The action of bromine gives rise to evolution of hydrobromic acid, and formation of a crystalline mass, insoluble in water, but dissolving in alcohol and ether, and containing probably $C_{18}\,H_{10}\,Br_3\,N$ (tribromocumidine). When exposed to the action of chlorate of potassa and

hydrochloric acid, it yields a brown body possessing the odour of chlorophenisic acid, which, treated with alcohol, leaves a substance resembling chlorokinone (chloranilè). Of the compounds, into which cumidine is converted by the influence of phosgene-gas and bisulphide of carbon, and which are most likely analogous to the aniline-terms described by Hofmann, Nicholson promises a more minute investigation. Cumidine.

Nitrocumidine.—Cahours(1) has converted binitrocumole $C_{18}\ H_{10}\ N_2\ O_8$ into the base corresponding to nitraniline. This substance, to which he assigns the name nitrocumidine, contains $C_{18}\ H_{12}\ N_2\ O_4 = C_{18}\ H_{12}\ (NO_4)\ N$. It forms yellow scales, fusing below 100°, which solidify on cooling into a radiated mass. It is insoluble in water, but dissolves readily in alcohol and ether, and is only partially decomposed on heating. Nitrocumidine has but a feebly alkaline reaction, but neutralizes the acids completely. The sulphate $C_{18}\ H_{12}\ N_2\ O_4,\ SO_3 + 2\ HO$ crystallizes in long brilliant prisms; the hydrochlorate $C_{18}\ H_{12}\ N_2\ O_4,\ HCl + HO$, as well as the nitrate and oxalate, form needles, whose solution, when exposed to the atmosphere becomes of a bluish-green.—Bromine converts nitrocumidine into a crystalline body, which is no longer basic. With chloride of benzoyl this base produces a compound, crystallizing from alcohol in needles. This substance, which contains $C_{32}\ H_{16}\ N_2\ O_6 = C_{14}\ H_5\ O_2,\ C_{18}\ H_{11}\ N_2\ O_4$ corresponds to benzamide and benzanilide. With the chlorides of cinnamyl and cumyl, Cahours has obtained analogous compounds.

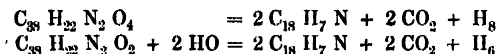
Cyanocumidine.—According to Hofmann(2), an alcoholic solution of cumidine, when treated with cyanogen-gas, deposits long needles of cyanocumidine. This base, which contains $C_{20}\ H_{13}\ N_2 = Cy,\ C_{18}\ H_{13}\ N$, is soluble in alcohol, and forms a very difficultly soluble salt with hydrochloric acid.

Cyanotoluidine has been obtained by Hofmann(3) by treating toluidine with cyanogen-gas; it is very difficultly soluble in alcohol and ether, and will, according to analogy, be represented by the formula $C_{16}\ H_9\ N_2 = Cy,\ C_{14}\ H_9\ N$.

(1) Compt. Rend. XXVI, 315; Instit. 1848, 71; J. Pharm. [3] XIV, 435.
(2) Loc. cit. p. 507.
(3) Ibid.

Chinoline.

Chinoline.—Laurent(1) considers the formula $C_{18}\,H_7\,N$ as probably true for chinoline or leucoline. Its formation from quinine and cinchonine accordingly would be represented by the equations:



$$C_{38}\,H_{22}\,N_2\,O_4 = 2\,C_{18}\,H_7\,N + 2\,CO_2 + H_8$$
$$C_{38}\,H_{22}\,N_2\,O_2 + 2\,HO = 2\,C_{18}\,H_7\,N + 2\,CO_2 + H_6$$

Picryl.—This substance which had been obtained by Laurent, in distilling oil of bitter almonds with sulphide of ammonium, and to which Berzelius (Jahresber. XXV, 631) had assigned the name *cripine*, contains, according to Laurent's first analysis $C_{42}\,H_{14}\,N\,O_4$. On repeating the experiment(2) he obtained 80·17—80·45 carbon, and 4·77—4·70 hydrogen; whence he proposes the formula $C_{42}\,H_{15}\,N\,O_4$, which requires 80.52 of carbon, and 4·78 of hydrogen. In chloro- and bromopicryl 1 or 2 equivs. of hydrogen are replaced by 1 or 2 equivs. of chlorine or bromine.

Lophine.—To this compound, prepared from hydrobenzamide by the action of heat, Laurent had formerly assigned the formula $C_{46}\,H_{17}\,N_2$. According to a more recent analysis(3), it contains 1 eq. of hydrogen less, having the composition $C_{46}\,H_{16}\,N_2$, (theory, 86·25 of carbon and 5·0 of hydrogen; experiment, 86·18—85·91 of carbon, and 5·10—5·14 of hydrogen).

Flavine.—Among the products of distillation of benzoate of lime, Chancel found a compound, benzophenone, isomeric with benzone, but crystalline, which contains $C_{26}\,H_{10}\,O_2$. When treated with nitric acid, this substance yields a yellowish crystalline powder, *binitrobenzophenone*, $C_{26}\,H_8\,N_2\,O_{10}$, which, under the influence of reducing agents, is converted into a basic compound, to which Chancel and Laurent(4) have given the name *flavine*. The product obtained in the dry distillation of benzoate of lime was freed from benzole and then boiled with fuming nitric acid for several hours; on addition of water to the nitric solution, a thick yellow oil was separated, which solidified partially after some time, and proved to be a mixture of several bodies, even after recrystallization. When dissolved in alcoholic or ethereal solution of sulphide of ammonium, it yielded flavine, which is deposited in needles. After purification (by

(1) Ann. Ch. Phys. [3] XIX, 367, (comp. p. 474).
(2) Ibid. 369, (comp. p. 474).
(3) Ibid. (comp. p. 474).
(4) Instit. 1848, 95; Laurent and Gerhardt's Compt. Rend. des Trav. Chim. 1849 91, 115.

Flavine. Constitution of the organic bases.

solution in hydrochloric acid and reprecipitation by means of ammonia), flavine forms colourless or slightly yellowish needles, insoluble in water, but dissolving in alcohol and ether, and yielding, when heated with solid hydrate of potassa, an oil of basic properties. Analysis gave 73·1 of carbon, 5·9 of hydrogen, and 13·5 of nitrogen, leading to the formula $C_{26}\,H_{12}\,N_2\,O_2$,—Hence the conversion of binitrobenzophenone into flavine is represented by the following equation:



$$C_{26}\,H_8\,N_2\,O_{10} + 12\,HS = C_{26}\,H_{12}\,N_2\,O_2 + 8\,HO + 12\,S.$$

The hydrochlorate, crystallizing in long plates, is readily soluble in water, less so in alcohol. The platinum-salt, when dried at 150°, contains $C_{26}\,H_{12}\,N_2\,O_2$, 2 H Cl, 2 Pt Cl_2, (theory, 31·43 per cent of platinum; experiment, 31·4).—Chancel considers flavine as identical with carbanilide, obtained by Hofmann(1) in studying the action of phosgene-gas on aniline; carbanilide, however, although having the same composition as flavine, possesses no basic properties.

For chloronicine and paranicine, we refer to p. 408.

Distinction of the Organic Bases by means of the Microscope.—According to Anderson(2), if to a dilute hydrochloric solution of one of the following bases, under the microscope of a magnifying power of 250, ammonia, or sulphocyanide of potassium be added, the following phenomena are observed, care being taken to avoid the use of too concentrated a solution:

	With ammonia.	With sulphocyanide of potassium.
Strychnine	Prismatic crystals directly.	Flat needles, truncated, or terminating in an acute angle.
Brucine	Stellated groups.	Delicate tufts.
Morphine	Rhombohedrons.	Amorphous precipitate.
Narcotine	Ramified crystals.	" "
Cinchonine	Stellated concentric needles, or grainy masses.	Six-sided crystals, mixed with irregular, flat, rectangular crystals.
Atropine	Amorphous mass.	

Constitution of the Organic Bases. — Fresenius(3) has enunciated the view, that the oxygenated organic bases, when containing

(1) Ann. Ch. Pharm. LVII, 267.
(2) J. Pharm. [3] XIII, 443.
(3) Ann. Ch. Pharm. LXI, 149.

Constitution of the organic bases.

more than 1 eq. of nitrogen, (f. i., strychnine, caffeine, &c.), independently of their formation, whether natural or artificial, have a constitution analogous to that of nitraniline; he considers them as simple bases (aniline, nicotine, sinammine), in which 1 eq. of hydrogen is replaced by an oxide of nitrogen, (NO, NO_2, NO_3, NO_4 and NO_5). A. W. Hofmann(1) has pointed out the arbitrary nature of this view, inasmuch as the existence of hydrocyanoharmaline, of cyaniline and the other collateral bases, discovered by Hofmann(2), prove that the second eq. of nitrogen may be present likewise, in the form of a cyanogen-compound.—Incidentally to his researches on melaniline, Hofmann gives a synopsis of all the facts supporting the view of Berzelius, that the organic bases are conjugated ammonia-compounds. In adopting this view, cyaniline, melaniline, &c., become conjugated bases of the second order, in which ammonia has assimilated various compounds, such as cyanogen, &c., in addition to the adjunct $C_{12}H_4$=An. The formulæ of these substances acquire thus the following shape,—

Aniline . .	NH_3 + An.
Cyaniline . .	NH_3 + An Cy.
Melaniline .	NH_3 + An_2, Ad, Cy.
Dicyanomelaniline	NH_3 + An_2, Ad, Cy_3.

(1) Ann. Ch. Pharm. LXVI, 148.
(2) Chem. Soc. Qu. J. I, 312; Ann. Ch. Pharm. LXVII, 166.

END OF VOL. I.

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